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THE USE OF COLLOID-ENHANCED ULTRAFILTRATION TO REMOVE ORGANIC POLLUTANTS AND METAL IONS FROM WASTEWATER GENERATED FROM THE PULP AND PAPER INDUSTRY

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By

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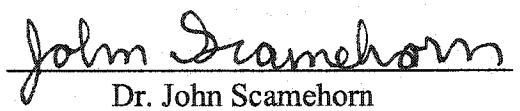
A Dissertation APPROVED FOR THE

SCHOOL OF CHEMICAL ENGINEERING AND

MATERIALS SCIENCE

By



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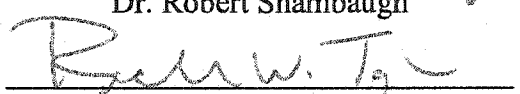

Dr. Richard Taylor

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ABSTRACT

Colloid – enhanced ultrafiltration (CEUF) is a surfactant based separation technique which requires low energy and produces high rejection with reasonable flux rates. In micellar-enhanced ultrafiltration (MEUF), surfactant at a concentration well above critical micelle concentration (CMC) is introduced into a given contaminated solutions. At a sufficiently high concentration, most of surfactant will be in micellar form. Polyelectrolyte micellar – enhanced ultrafiltration (PE-MEUF) is a modified MEUF technique in which a mixture of a surfactant and an oppositely charged polymer mixture is used as a colloid. The colloid can have a net negative charge if an excess amount of the polymer is used. Pollutants can associate with colloids: surfactant micelles or surfactant – polymer aggregates solubilize organic solutes and metal ion binds to the negatively charged surfactant – polymer aggregates. The studies herein investigate the application of MEUF and PE-MEUF for the removal of ionizable organic solutes (chlorophenols) and metal ions. Higher organic solute removal is observed in MEUF than in PE-MEUF for all systems studied. However, surfactant leakage is significantly reduced in PE-MEUF, as compared to MEUF. For chlorophenols with a higher degree of chlorination (low water solubility), high rejections are reported in both MEUF and PE-MEUF. When the organic solute is deprotonated, the solubilization in the micelles is enhanced due to ion-ion interaction between the cationic surfactant head group and the phenolate anion. The effect of added salt on the solubilization and surfactant leakage is investigated in both MEUF

and PE-MEUF. Added salt enhances the solubilization and reduces the surfactant leakage in MEUF, whereas it decreases the solubilization and increases the surfactant leakage in PE-MEUF. Surfactant – polymer aggregates are shown to be effective in the simultaneous removal of an organic solute and a metal ion. The effects of surfactant and polymer concentrations as well as surfactant to polymer concentration ratio are all important. Ultrafiltration experiments are used to determine the effect of salt on gel point (the point at which flux becomes zero) for PE-MEUF.

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CHAPTER 1

INTRODUCTION

Highly toxic and persistent chlorinated dibenzo-p-dioxins, dibenzofurans, and chlorinated phenolic compounds are formed during pulp bleaching when chlorine and chlorine derivatives are used and can be found in wastewater from pulp and paper mills. Chlorinated phenols are known 'as precursors of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), highly toxic and bioaccumulative matters[1]. In Canadian bleached pulp mill effluents[2], seventy to eighty percent of dissolved matter consists of high molecular weight chlorinated organic compounds ($MW \geq 1000$). These compounds can be microbiologically transformed or degraded into low molecular weight compounds that add to the total low molecular weight loading. The low molecular weight compounds simply pass through biological membranes[3-4] and accumulate in rivers and oceans, leading to aquatic toxicity. Generally, compared to compounds with a lower degree of chlorination, highly chlorinated compounds or meta-chlorinated compounds are more stable and more persistent in the aquatic environment[5-6]. A principal chlorinated phenol in bleached

sulphite discharges is 2,4,6-trichlorophenol[7]. Also 2,4-dichlorophenol together with a number of chlorinated phenolic compounds are produced in significant quantity[8].

Total Chlorine Free (TCF) and Elemental Chlorine Free (ECF) bleaching can be used to reduce or eliminate the formation of wastewater pollutants; however, lower product quality[9] and heavy capital investment[10] are associated with these non-chlorine bleach technologies. Therefore, instead of "in-process technological changes" (i.e., TCF or ECF), end-of-pipe wastewater treatment can be used to remove pollutants formed during chlorine treatment. Ultrafiltration (UF) processes can be used to effectively treat the wastewater generated in the alkaline stage (E-stage) from bleach kraft pulp mills[11]. Nonetheless, the wastewater generated in the acid stage, which contains mostly low molecular weight substances, cannot be efficiently treated with this technique[12].

Colloid-enhanced ultrafiltration (CEUF) methods[13-42] are novel separation processes for removing organic solutes and metal ions from aqueous streams. Micellar-enhanced ultrafiltration (MEUF)[13-31] is one technique in which a micellar solution is added to a contaminated feed solution. Polymer micellar-enhanced ultrafiltration (PE-MEUF) is a modified MEUF technique where a surfactant - polymer mixture is used in the colloid solution[42-45]. This solution is then passed through a membrane, which has pores small enough to block the passage of micelles or surfactant - polymer complexes, removing the surfactant aggregates and solubilized organic solute. It has been shown that the concentration of solute in the permeate (solution passing through the membrane) is approximately that expected if the system

were at equilibrium[15-18]; i.e., the permeate concentration is equal to the unsolubilized solute concentration in the retentate. Therefore, equilibrium solubilization measurements (for example using semiequilibrium dialysis or SED[42, 44-49], or vapor pressure techniques[43, 50-51] can predict rejection of solutes in MEUF.

The studies presented in this work evaluate MEUF and PE-MEUF to remove chlorophenols from aqueous solutions. Chapter 2 presents an overview of background information that are necessary to appreciate the material covered in this dissertation. Chapter 3 focuses on comparison of process efficiency between MEUF and PE-MEUF. Solubilization constant and surfactant leakage are the main parameters used for comparison. Effect of organic solutes with variable degree of chlorination is also discussed in this chapter. Due to the fact that the solutes of interest are ionizable, the next study in Chapter 4 is then an investigation of the acid dissociation constants of the chlorophenols in colloid solutions in both the presence and absence of salt. Distribution coefficients of both ionized and neutral species are reported here. The distribution coefficient results help to understand the solubilization behavior in colloid solutions at different pHs. In Chapter 5, the effect of salinity on solubilization constants of the solutes is investigated whereas Chapter 6 talks about the effect of salinity on surfactant leakage. The last study was designed to explore the possibilities of applying PE-MEUF to simultaneously remove an organic solute and a divalent metal ion from an aqueous stream. This work is presented in Chapter 7. Finally, Chapter 8 summarizes the conclusions from this study and perspectives on future work on this field.

CHAPTER 2

BACKGROUND

The research work presented in this dissertation is relevant with several research areas. Therefore, basic information necessary to comprehend the work presented in Chapter 3-7 of this dissertation are discussed in this chapter as follows: (1) micelle formation by surfactant, (2) colloid-enhanced ultrafiltration, (3) surfactant - polymer interaction, and (4) solubilization of dissolved organic solutes.

2.1 Micelle Formation by Surfactant

2.1.1 Surfactant Background

Surfactants are characterized by the presence of two moieties in the same molecule, one polar and the other non polar. The polar group may carry a positive charge or negative charge, giving rise to cationic or anionic surfactants, or may contain ethylene oxide chains, as in the case of nonionic surfactant. The nonpolar part of the molecule is generally a hydrocarbon chain, but may contain aromatic groups. The existence of groups with opposing characteristics is responsible for all the special properties of surfactants. The behavior of surfactants in aqueous solution is determined by their tendency to seclude their hydrophobic part from solution and

expose their hydrophilic part towards the solution. This dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates as micelles.

2.1.2 Micelle Formation

Micelles are aggregates containing 50 to 100 surfactant molecules, which form in a surfactant solution at a concentration above critical micelle concentration (CMC). These micelles form such that the tail groups orient themselves far away from the bulk aqueous solution and cooperatively interact with each other by hydrophobic interaction; therefore, surfactants with a longer hydrophobic chain tend to form micelle more favorably and with a lower CMC than surfactant with a shorter tailgroups[52]. The surface of the micelle consists of the hydrophilic head groups extended towards the aqueous environment. Primarily, charged headgroups will tend to repel each other at the micellar surface, leading to higher relative CMC values for ionic surfactants than those for associated nonionic surfactants[53-54]. Therefore, the CMC of a given ionic surfactant is lowered by increasing counterion binding, resulting in decreased electrostatic repulsion between head groups. A micellar property of particular importance to many fields of studies, including the development of separation techniques, is solubilization, which will be discussed later on in this chapter.

2.1.3 The CMC Dependence on Chemical Structure

Several general remarks about the variation of the CMC with the surfactant chemical structure can be made as follows[55]:

(i) The CMC strongly decreases with increasing alkyl chain length of the surfactant. As a general rule, the CMC decreases by a factor of ca. 2 for ionic surfactants (without added salt) and by a factor of ca. 3 for nonionic surfactants on adding one methylene group to the chain.

(ii) The CMCs of nonionic surfactants are much lower than those of ionic surfactants. The relationship depends on alkyl chain length, although two orders of magnitude is a rough starting point.

(iii) Cationic surfactants typically have slightly higher CMCs than anionic surfactants. For nonionic surfactant of the oxyethylene variety, there is a moderate increase of the CMC as the polar head group become larger.

2.1.4 Structure of Micelles

Micelles in aqueous solutions have essentially a "hydrocarbon-like" interior and hydrophobic groups on the outside. Well-studied micelles like those of SDS have a near-spherical geometry over a wide-concentration range above the CMC. In most cases, there is no major change in shape until the surfactant approaches the solubility limit, where a liquid crystalline phase normally separates out. In certain cases,

however, formation of larger micelles with increase in concentration above the CMC has been reported. In case of ionic surfactants, some of counterions are bound strongly to the so-called "Stern layer" of the charged surface[56]. About 70% of the total micellar charge is neutralized by the ions in the Stern layer and the rest by the counterions in the Gouy-Chapman electrical double layer. The region within micelle, but very close to the polar head, is often referred to as the palisade layer.

2.1.5 Micellar Shape and Aggregation Number

Israelichvili et al.[57] developed a detailed theory of aggregation in surfactant solutions taking into account the shape and size of surfactants. They define a critical linear dimension l_c which is less than the length of hydrocarbon chain or the radius of a spherical micelle (R) with no hole in the core. Their analysis leads to the conclusion that l_c is related to the shape, volume (v), and the surface area (a). For a linear chain, Tanford[58] has obtained the following relationships for the hydrocarbon chain volume (v), and the critical length (l_c):

$$v = 27.4 + 26.9\, nA^3 \qquad (2.1)$$

$$l_c = 1.5 + 1.265\, nA^2 \qquad (2.2)$$

where n is the number of carbon atoms in the chain. For a fully extended saturated chain, l_c may be 80% of the chain length. The total volume of aggregate (V) and surface area (A) are related by: $V/v = A/a = N$, the aggregation number of the micelle.

Surfactant with bulk hydrophilic groups and long, thin hydrophobic groups tend to form spherical micelles in aqueous solutions whereas surfactants with bulky hydrophobic groups and small hydrophilic groups tend to form lamellar or cylindrical micelles. As mentioned earlier, the shape of micelle is related to its size. The size is usually expressed in terms of an aggregation number which can be determined by many methods such as scattering techniques. Size and aggregation number of surfactants change noticeably with such variables as ionic strength and temperature.

2.2 Physical Chemistry of Polymers

The term polymer refers to molecules of which the mass exceeds a few thousand daltons. The size places polymers over the range of size scales from atomic molecular to colloidal. Polymers are covalently bonded strings of atoms; as such, they physically connect and interact with spartially separated regions in a solution[59]. Polyelectrolytes are polymers bearing dissociated ionic groups. Polyelectrolyes partially dissociate in aqueous solution into polyions and small ions of opposite charge, known as counterions[60]. With highly charged polymer chains, the spatial distribution of charge is strongly inhomogeneous. The high charge density along the polymer chain produces a high electrostatic potential around it, and a fraction of counterions is consequently located in the immediate vicinity of the polymer chain; this phenomenon is called counterion condensation[61-62]. Repulsion between charged segments of a polymer can be of long range and can affect the configuration of a

polymer. Common polymers are those based on sulfonate, phosphate, carboxylate, pyridinium, or charged peptide groups incorporated into a polymer[63].

High charge density can effectively straighten the chain into a rod. The polymer conformation changes from a contracted coil to an expanded rod with increasing charge[60,64]. The amount of dissolved salt in the solution, which can screen the electrostatic repulsion, and the linear density of charged groups along the chain backbone are principle determinations of the chain configuration. The expansion of polymer chains due to charge repulsion is most often described in terms of the persistence length[65-66].

2.3 Surfactant - Polymer Interaction

The case of surfactant - polymer pairs in which the polymer is a polyion and the surfactant is also ionic but bears the opposite charge is of special interest. When the respective charges are of the same sign, association between the polymer and the surfactant can be expected to be feeble or absent[67]. Association between most polymers and surfactants follows a similar pattern, that is, micelles or aggregates form on polymer chains at concentration lower than the critical micelle concentration (CMC) in pure solution. This often arises from a lowering of repulsion between surfactant head groups or the hydrophobic nature of polymer chains providing additional stabilization for the micelle. It is rare for surfactants to bind as separate, individual molecules to a polymer chain, even where the polymer and surfactant have

opposite charges. Surfactant molecules do bind individually to some hydrophobically modified polymers, where there is a relatively stable hydrophobic region already formed from the side-chains of the polymer[67]. Surfactant binding to polymers in aqueous solution has been investigated extensively[67-88].

In the absence of polymer, surfactant molecules aggregate in aqueous solutions to form spherical, globular or rodlike, etc., at concentration beyond a critical micelle concentration. The nature of the surfactant head groups and tail groups determines which type of aggregate structure would form, what would be the average size, and magnitude of CMC. When a polymer is added to the aqueous solution, singly dispersed polymer molecules as well as intermolecular complexes between the polymer and the surfactant can also be present. One class of studies concerns the morphology of surfactant - polymer complexes in solution. Techniques such as nuclear magnetic resonance (NMR), neutron scattering, and fluorescence spectroscopy have been used to elucidate the structure of surfactant-polymer complexes and to estimate the size of the polymer-bound micelles. The second type of investigations has involved the quantitative measurement of the amount of surfactant associating with the polymer molecules; also, the occurrence of critical phenomena in solution properties has been examined. For these studies, classical techniques such as dialysis, surface tension, viscosity, electrical conductivity, dye solubilization, etc., have been employed. The third class of investigations has focused on the phase behavior of surfactant-polymer solutions. Results from these studies show that some surfactants do not associate at all with polymers while others do so significantly.

2.3.1 Driving Forces

The interaction responsible for association phenomena in surfactant - polymer systems are mainly[89]:

1. Hydrophobic interaction between polymer and surfactant molecules; this interaction will be particularly important for block copolymers with hydrophobic segments or for so-called hydrophobe-modified polymers

2. Hydrophobic interaction between surfactant molecules

3. Hydrophobic interaction between polymer molecules

4. Electrostatic interactions between polymer molecules

5. Electrostatic interactions between polymer and surfactant molecules; these may be attractive or repulsive, depending on whether the molecules have similar or opposite charges

6. Electrostatic interactions between surfactant molecules; these repulsive interactions are strongly unfavorable for surfactant micellization and a modification of them due either to amphiphilic portions of a polymer chain ("dilution effect") or to the net charges of a polyion (neutralization) can dramatically facilitate surfactant self-assembly.

Of the different interactions mentioned, the main driving force for association in surfactant - polymer systems in general comes from the hydrophobic interactions between surfactant molecules. Because of delicate energetical balance, even quite small modifications of the free energy of normal micellization and small contributions

from the other interactions can have dramatic influences on the self-assembly and induce important surfactant - polymer interactions.

2.3.2 Surfactant Binding and Self-Assembly

Binding has generally to be considered to involve a certain degree of "cooperativity"; typically the inferred cooperativity is very high. The interaction is discussed in terms of the binding of the surfactant molecules to the polymer chains and binding is characterized by an equilibrium constant for binding to specific sites. As mentioned above, the dominating force in surfactant - polymer systems is the hydrophobic interaction among the surfactant chains. Therefore, a starting point of discussions of surfactant - polymer interaction appears to be to consider the effect of polymer molecules on surfactant self-assembly, notably micelle formation.

As of "binding" approach, it is informative to obtain binding isotherms which present the concentration of polymer-bound surfactant as a function of the surfactant activity (free surfactant unimer concentration) or total surfactant concentration. Binding isotherms are particularly appropriate for the case where the polymer affects surfactant self-assembly through short-range interactions. Then a plateau value and a saturation of binding result, and the formation of free micelles starts at a certain concentration above the saturation concentration, resulting in coexistence of free and polymer-bound micelles.

A typical binding isotherm has a marked sigmoidal shape, which is an indication of cooperative binding, and the onset of surfactant binding often occurs at a certain surfactant concentration called the critical aggregation concentration or "cac". The cac indicates that the surfactant molecules form aggregates upon interacting with polymer chains[90]. In general, a steep binding isotherm (a large cooperativity) is expected if the polymer-adsorbed surfactant molecules form micelles which are similar to normal free micelles. Sometimes, the free surfactant concentration at the midpoint of the binding isotherm is used instead of the cac to characterize the interaction. For a highly cooperative binding, there will be little difference between this value and the cac.

The leveling out of the binding isotherm at higher surfactant concentrations is due to saturation of the polymer with surfactant and indicates the maximum amount of surfactant that can be bound per polymer unit. For many systems, this level is not reached due to phase separation or obscured by the formation of free micelles.

2.3.3 Surfactant - Polymer Association Structure

Various morphologies of surfactant - polymer complexes can be visualized, depending on the molecular structures of the polymer and the surfactant and on the nature of the interaction forces operative between the solvent, the surfactant, and the polymer[91]. A schematic view of these morphologies is presented in Figs. 2.1 through 2.8. Structure in Fig. 2.1 denotes that no polymer-surfactant association occurs. This

could arise in a situation where both the polymer and the surfactant carry the same type of ionic charges. This could also occur when the polymer is relatively rigid and for steric reasons does not interact with ionic or nonionic surfactants. It could also be the situation when both the polymer and the surfactant are uncharged and no obvious attractive interactions, promoting association, exists between them. Structure in Fig. 2.2 denotes a system where the polymer and the surfactant carry opposite electrical charges. Their mutual association is promoted by electrostatic attractions. This causes the creation of a complex with reduced charge and hence reduced hydrophilicity. This eventually leads to the precipitation of these complexes from solution. Structure in Fig. 2.3 also occurs in systems containing surfactant and oppositely charged polymer. In this case, the surfactant promotes intramolecular bridging within a polymer molecule by interacting with multiple sites on one molecule or intermolecular bridging by interacting simultaneously with sites on different polymer molecules.

Structure in Fig. 2.4 depicts a situation when the polymer is a random copolymer or multiblock copolymer with relatively short blocks. In this case, the surfactant molecules orient themselves at domain boundaries separating the polymer segments of different polarities. Depending upon whether the polymer is a random copolymer or a block copolymer, the segregation in the polymer can take different forms, including the formation of polymeric micelles.

Structures in Figs. 2.5-2.7 pertain to hydrophobically modified polymers[91-92]. In this case, the size of the hydrophobic modifier, its grafting density along the

polymer, and the relative concentrations of the surfactant and the polymer influence the nature of the association structure. In general, at low surfactant concentration, structure in Fig. 2.5 may be obtained with single surfactant molecules or very small surfactant clusters interacting with one or more hydrophobic modifiers, without causing any conformational changes on the polymer. When the surfactant concentration is increased, somewhat larger surfactant clusters form co-aggregates with multiple hydrophobic modifiers belonging to the same polymer molecule, causing the polymer conformation to change significantly as depicted in Figure 2.6. At larger surfactant concentrations, it is possible to obtain the structure in Figure 2.7 where surfactant aggregates are formed around each of the hydrophobic modifier.

Structure in Fig. 2.8 denotes a complex consisting of the polymer molecule wrapped around surfactant micelles with the polymer segments partially penetrating the polar head group region of the micelles and reducing the micelle core-water contact. A single polymer molecule can associate with one or more surfactant micelles. Such a structure can describe a nonionic polymer interacting with surfactant micelles. Such a structure can also be imagined in the case of an ionic polymer interacting with oppositely charged micelles.

2.3.4 Polymers and Oppositely Charged Surfactants

Systems of a polymer and an oppositely charged surfactant have been extensively studied in dilute solution. Due to strong attraction between the two

species, the interaction starts at very low surfactant concentrations. Kwak and coworkers have made intensive studies[69-73,75] of binding of cationic surfactant to a series of anionic polymer under a variety of conditions, e.g. added salt concentration, salt type and temperature. The cationic surfactant comprises of alkyl (C_{11} and C_{14}) trimethylammonium bromide and alkyl (C_{11}, C_{12}, C_{13}, C_{14}) pyridinium bromide. The polyanion series comprises of sodium dextran sulfate (SDexS), polystyrenesulfonate (PSS), etc. Their binding data are of high precision in view of the excellent performance of the surfactant-ion-selective electrodes.

Binding of a cationic surfactant to polyanions starts at a concentration which is several orders of magnitude lower than the CMC in polymer-free solution. The surfactant binding is highly cooperative in these systems, indicating interaction among the absorbed surfactant molecules and the formation of polymer-absorbed micelles or micelle-like clusters. The major reason for cooperative binding of surfactant molecules to an oppositely charged polymer is the electrostatic stabilization of the surfactant micelles. We may thus picture surfactant "binding" to polymer as counterion binding of the polymer charges to the surfactant micelle.

Influence of surfactant : the length of hydrocarbon tail of the surfactant is a crucial parameter for the interaction with a polymer[93]. It was observed that the interaction is enhanced for a surfactant of longer hydrocarbon tail. This can be attributed to the uneven distribution of counterions between the bulk and the micellar surface, which is unfavorable for the formation of normal micelles and which is more pronounced for a longer surfactant. A second way of conceiving the interaction is to

consider the concentration of ion or electrolyte in the solution. A lower CMC gives a lower electrolyte concentration, therefore stabilizing the polymer-bound micelles. It can be noted that for surfactants with less than a certain number of carbons in the alkyl chain, there will be no binding to the polymer[94]. In other words, normal micelles are favored relative to the polymer-bound micelles.

Influence of polymer : The properties of the polymer are also of important for the surfactant - polymer interaction. One important parameter is the reduced linear charge density of the polymer, ζ, which is related to the distance, b, between adjacent charges along the polymer backbone by the relation

$$\zeta = e^2/4\pi\varepsilon bkT \qquad (2.3)$$

where e is the magnitude of the electrostatic charge, ε is the dielectric constant of the solvent, and kT is the product of the Boltzman constant and the absolute temperature. It was found that an increase in linear charge density gives rise to a stronger interaction, resulting in a decrease in the cac[94]. In addition, different types of charged groups on the polymer, the flexibility of the polymer backbone, and the type of counterions present influence the interaction. The influence of hydrophobic groups in the polymer chain was investigated using copolymers of maleic acid and different vinyl ethers[95]. It was found that the interaction is enhanced by a larger size of the hydrophobic group. In addition, the interaction is stronger at a lower degree of neutralization of the polyacids[95].

Effect of salt : Several investigators have studied the effect of salt in dilute systems of polymer and oppositely charged surfactant[69,71,74, 75,93,96-97]. Almost all

results show that the critical aggregation concentration increases with increasing simple salt concentration. This indicates that the interaction between polymer and surfactant is reduced by addition of salt. The effect of salt on the surfactant - polymer complexes is thus opposite to the influence of salt in micellar systems, where stabilization occurs, manifested by a lowering of the CMC[98-99]. At high concentration of added salt, this effect will also dominate in surfactant - polymer systems. The effect of salt is thus twofold: (1) reduction of the electrostatic interaction between the surfactant and the polymer, and (2) stabilization of the surfactant aggregates. The first mechanism will dominate at low ionic strength whereas at high ionic strength, the second mechanism will take over. A decrease in the cac at high salt concentration, similar to the CMC behavior, can therefore be expected. The effect of added salt can also be discussed in terms of the cooperativity of the surfactant binding[93]. An increase in the cooperativity parameter, u, is observed when salt is added to the systems. This is due to (1) the screening of the repulsion between the polymer-bound micelles, and (2) the polymer-bound micelles being more similar to ordinary micelles on addition of salt.

2.4 Ultrafiltration (UF)

Ultrafiltration classified as pressure driven membrane separation technique is an attractive industrial separation method for removing molecule from water; however, traditional ultrafiltration is not effective in removing solutes with molecular

weight less than 500 daltons[100]. Ultrafiltration membranes generally retain intermediately sized particles between 10 Å and 200 Å in radius[101]. Modern ultrafiltration membrane have an anisotropic structure. These membranes are capable of rejecting solutes varying from 300 to 300,000 daltons, or molecular weight cut-off (MWCO), based on a globular protein[101].

2.4.1 Colloid-Enhanced Ultrafiltration (CEUF)

A new class of ultrafiltration techniques has been developed at Institute for Applied Surfactant Research, University of Oklahoma, called colloid-enhanced ultrafiltration (CEUF). All techniques involve adding a water-soluble colloid such as surfactant, polymer, and surfactant – polymer mixture to a feed stream containing target pollutants. The resulting solution is passed through an ultrafiltration membrane with pore sizes small enough to block the passage of the colloid. CEUF processes can be categorized as follows: micellar-enhanced ultrafiltration (MEUF), polyelectrolyte-enhanced ultrafiltration (PEUF), ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), ligand-modified polyelectrolyte-enhanced ultrafiltration (LM-PEUF), ion-expulsion ultrafiltration (IEUF), and polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF).

MEUF utilizes surfactant micelles to solubilize target molecules, and the solubilization molecules are forced to remain in the retentate solution because the micelles are too large to pass through the membrane[13-31]. Target pollutants for the

MEUF are particularly ionic species and organic solutes. Ionic solutes are bound electrostatically to the oppositely charged micellar surface whereas hydrocarbor organic solutes solubilize in the micellar core. PEUF can also be used to remove ionic species by using oppositely charged polymer[32-37]. An inherent problem in using conventional CEUF, including MEUF and PEUF, for removal metal cations such as lead (Pb) is that there is no selectivity in the process except on the basis of the valency of the cations. All divalent cations, such as Mg^{2+}, Ca^{2+}, and Pb^{2+}, are removed to essentially the same extent[32]. As a result, the application of CEUF for the selective removal of divalent cations has been developed, which is ligand-modified colloid-enhanced ultrafiltration (LM-CEUF). LM-CEUF utilizes derivatized agents that selectively bind a target metal ion and then solubilize in or bind to a colloidal pseudophase. LM-MEUF requires a ligand that consists of a chelating group with a long hydrocarbon tail. Such ligands are able to bind a target metal ion and then solubilize into the hydrophobic interior of surfactant micelles[40-41]. Alternately, in LM-PEUF, ligands are designed to bind target metal ions and carry a multivalent anionic charge. These multivalent ligand - metal complexes can then be electrostatically bound to cationic polymers[38-39]. IEUF involves the use of colloid which has the same charge as the target ion. The target ion is concentrated in the permeate stream as a result of ion expulsion, and the colloid remains in the retentate[102-103]. The polymer-surfactant complexes can solubilize organic solutes with approximately the same level as micelles, per surfactant molecule[45]. Use of these polymer-surfactant mixtures instead of surfactant alone in the ultrafiltration process is called polyelectrolyte

micellar-enhanced ultrafiltration or PE-MEUF, depicted in Fig. 2.9. It has been shown that surfactant - polymer complexes retain the ability of the surfactant to solubilize hazardous organic solutes, with substantial reduction of surfactant loss through the ultrafiltration membrane[42, 44].

2.4.2 Solute Rejection

Due to the primary separation mechanism in ultrafiltration, the retention of solutes is a key parameter to determine the process efficiency. Neither low molecular weight organics nor non complexes metal ionic species can be effectively removed using direct ultrafiltration. Therefore, the process efficiency can be qualitatively determined by a parameter called "rejection". A retentate-based rejection (in %) is defined as[18]:

$$\text{Solute rejection (\%)} = (1 - \frac{C_{A,perm}}{C_{A,ret}}) * 100 \qquad (2.4)$$

where $C_{A,perm}$ and $C_{A,ret}$ are the concentration of solute A in the permeate and the retentate solutions, respectively.

2.5 Solubilization of Dissolved Organic Compounds

The solubilization of organic solutes by surfactant micelles is relevant in many fields, such as detergency[104], colloid-enhanced ultrafiltration[13-21,45-46,48-51], and enhanced-oil recovery[105-106]. It can also served as a basis to understand biological

phenomena like those taking place in hydrophobic environments near water interfaces, including membranes and enzymes. General features of micellar solubilization were established early by McBain, Klevens, Hutchinson, Elworthy [107-111]. McBain and Hutchinson have developed the concept of solubilization in solutions that would have contained micelles.

Usually the solubilization of non polar solute is different from that of polar solute. The solubilization of organic solute is believed to occur at a number of different sites in the micelle, as shown in Fig 2.10; 1) on the surface of the micelle, at the micelle – solvent interface; 2) in the polar/ionic outer region (so-called palisade layer) of the micelle, between the hydrophilic groups and the first few carbon of the micelle[112] (3) in the non polar/inner region or hydrophobic region. The locus of solubilization varies with the chemical nature of the solubilized solute and the micelle, and it also reflects the type of interaction occurring between the specific parts of the surfactant micelle and the solute. Generally, saturated aliphatic and cyclic hydrocarbons and other types of non polar molecules are solubilized in the inner core region of the micelles. Polar solutes such as alcohols or polar aromatic compounds are believed to be solubilized between the individual molecules of surfactant in the polar/ionic outer region of the micelles, with the polar groups of the solute oriented toward the polar groups of the surfactants and the non polar portions of the solute oriented toward the core side of the micelle. A major part of the interaction of the solute molecule in this region is presumably by hydrogen bonding and dipole-dipole or ion-dipole attraction between the polar groups of the solute and surfactant. The

degree of penetration of polar solute molecule into the interior of the micelle depends on the relative extent of polar and nonpolar regions in the solute molecule, so that long-chain and less polar solutes will penetrate more deeply than shorter-chain and more polar compounds. Therefore, the polarity and hydrophobicity of solute molecules will influence the extent of solubilization and the solubilization sites within a given surfactant micelle.

Many factors, such as structure of the surfactant, the nature of the electrolyte, monomeric organic additives, polymeric organic additive, and temperature can affect the extent of solubilization and the locus of the solute in the micelle. Generally, the presence of solubilized organic additives in the micelle can change the solubilization of organic solutes. Several research studies[113-115] have been done to see the effects of monomeric organic additives on the solubilization of organic solutes in ionic micelles. The organic additives can be categorized into two type: non polar hydrocarbons such as alkanes and polar compounds such as long-chain alcohols.

A solubilized non polar hydrocarbon causes the micelle to swell; this may enhance the solubilization of polar solutes near the surfactant head groups. On the other hand, the solubilization of polar additives such as medium chain length alcohols appears to decrease the solubilization of other polar organic solutes in the same micelle. These effects are believed to arise from the competition between the polar solute and the polar organic additive for sites in the hydrophilic polar/ionic outer region of the micelle.

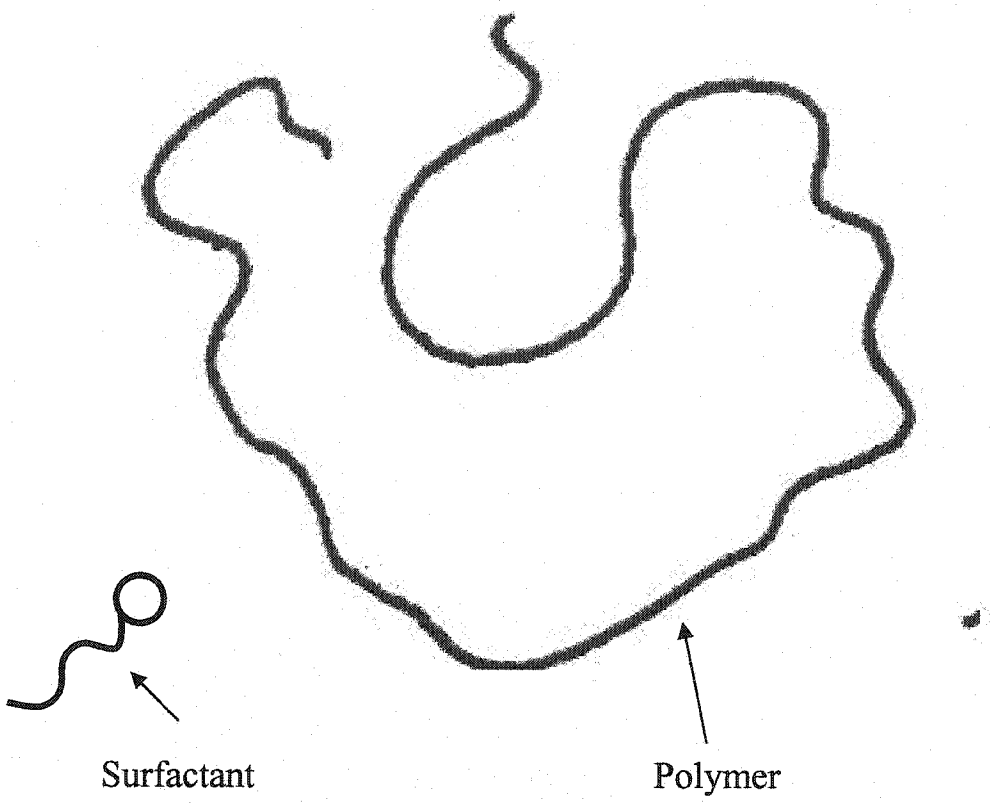


Figure 2.1 Surfactant-polymer structure when the surfactant and the polymer are both cationic or both anionic. Polymer molecule does not interact with surfactants.

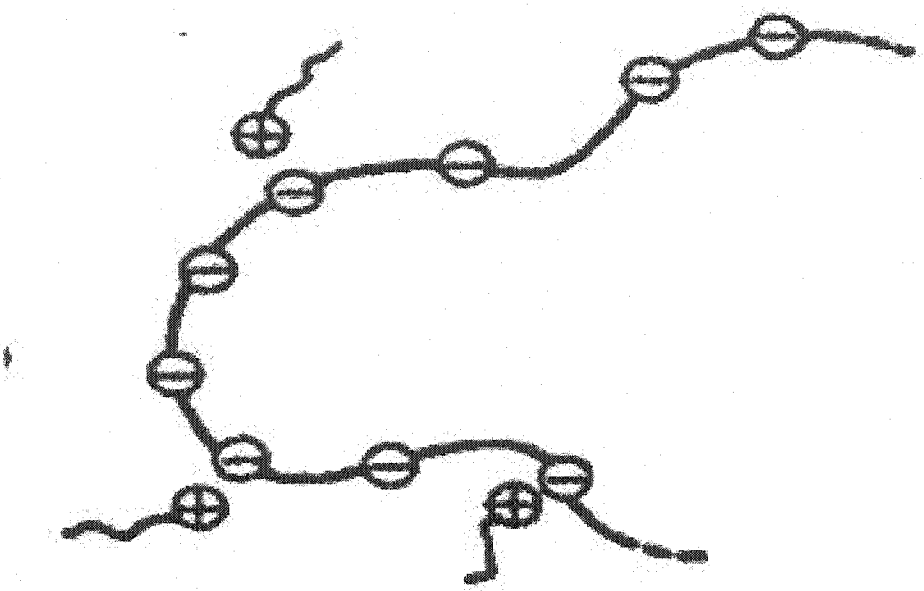


Figure 2.2 Surfactant – polymer structure when the polymer and the surfactant are oppositely charged. Single surfactant molecules are bound linearly along the length of the polymer molecules.

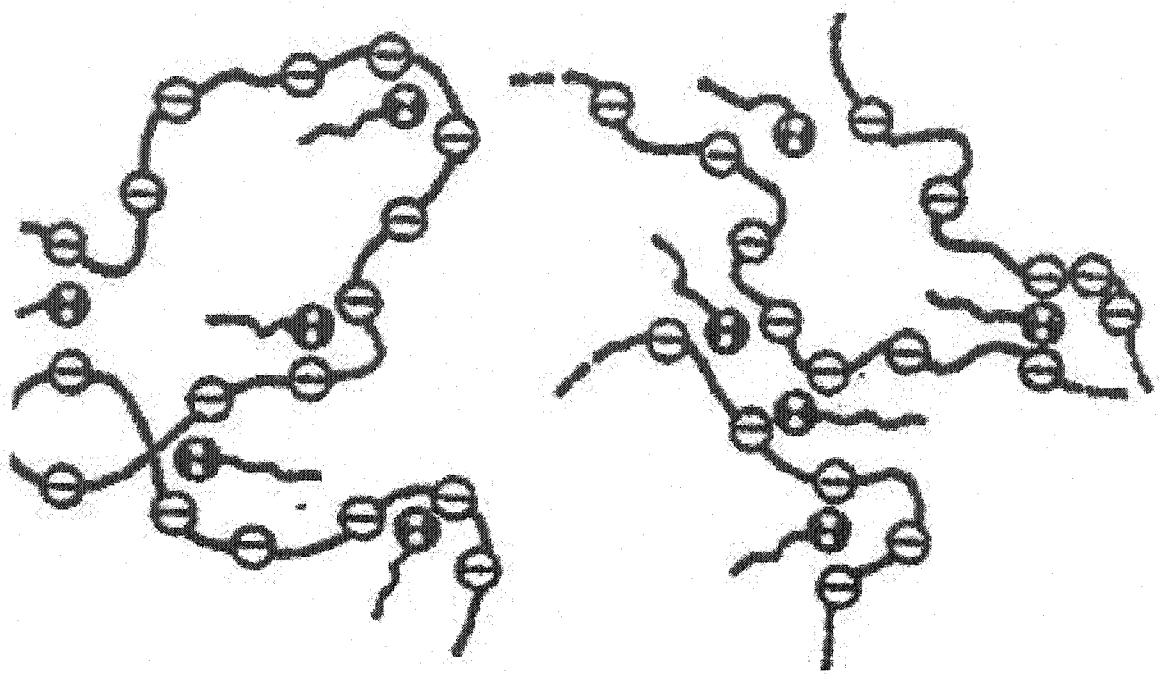


Figure 2.3 Surfactant – polymer structure when the polymer and the surfactant are oppositely charged. A single surfactant molecule binds at multiple sites on a single polymer molecule.

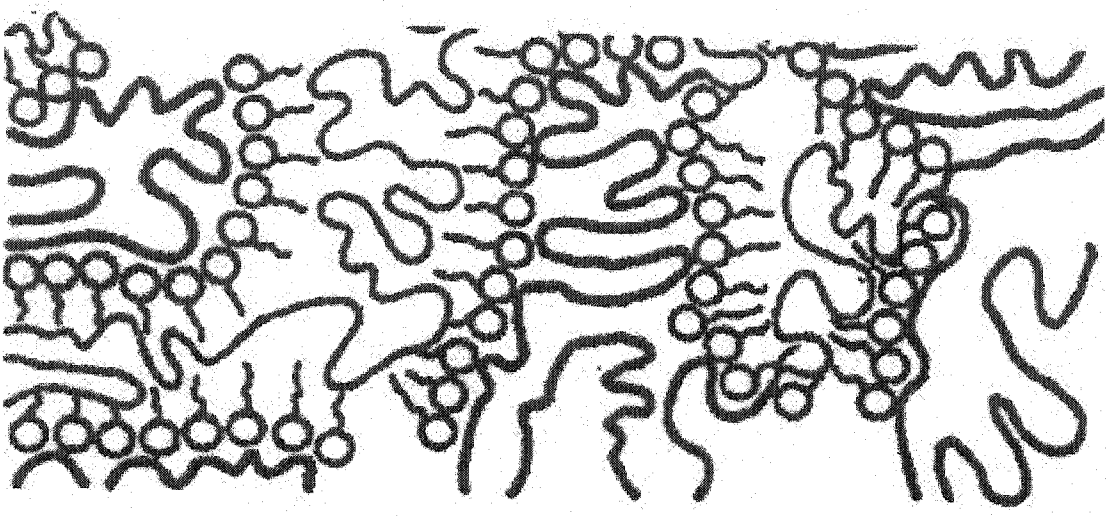


Figure 2.4 Surfactant – polymer structure when the polymer is an uncharged random or multiblock copolymer.

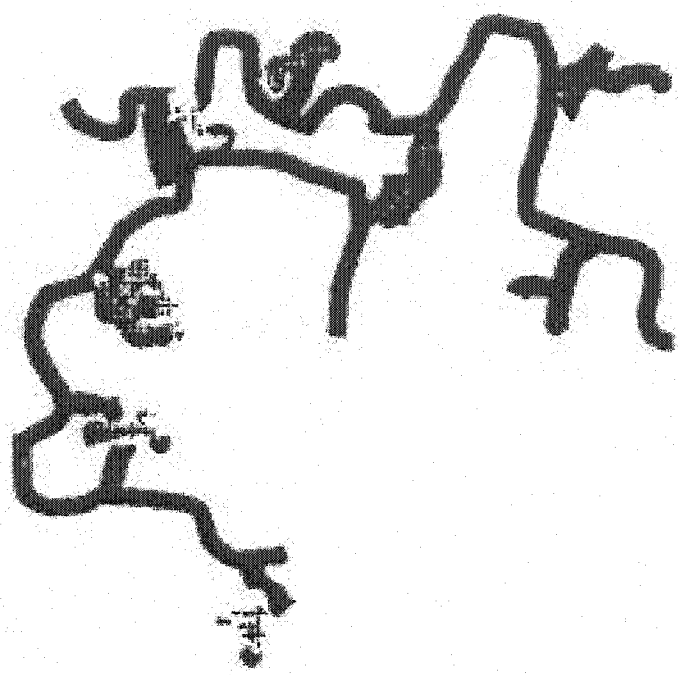


Figure 2.5 Surfactant – polymer structure when the polymer is hydrophobically modified. Individual surfactant molecules associate with one or more of the hydrophobic modifiers on single or multiple polymer molecules.

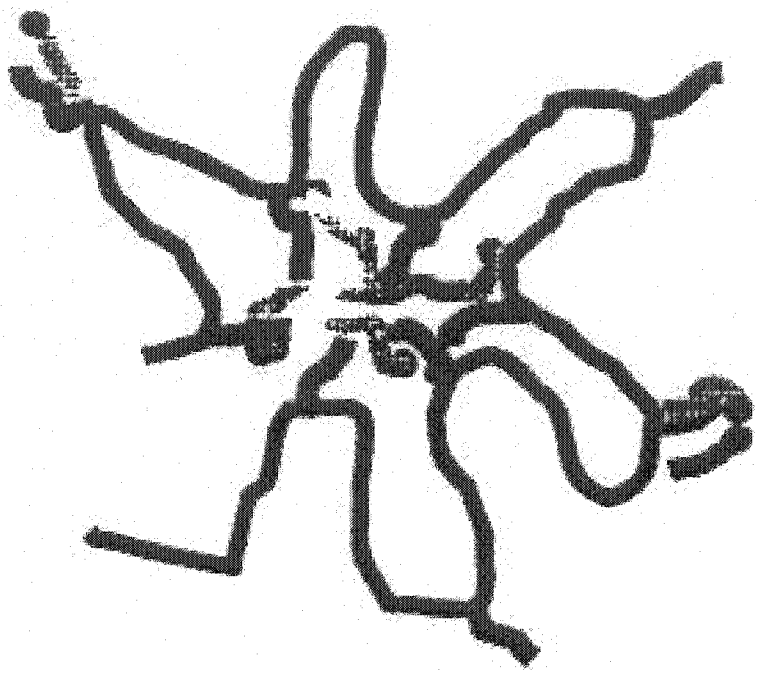


Figure 2.6 Surfactant – polymer structure when the polymer is hydrophobically modified. Clusters of surfactant molecules associate with multiple hydrophobic modifiers on a single polymer molecule.

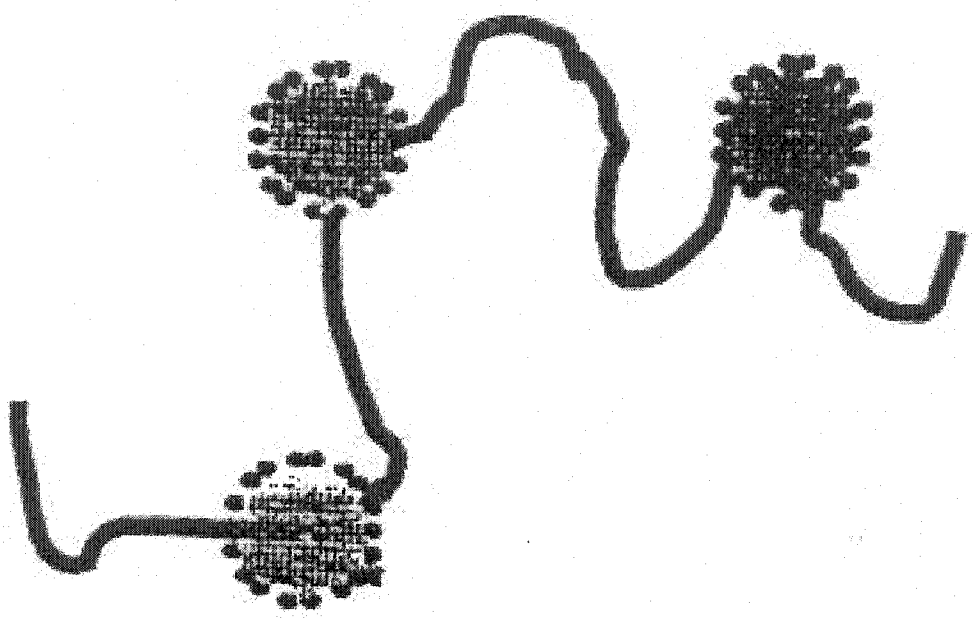


Figure 2.7 Surfactant – polymer structure when the polymer is hydrophobically modified. Clusters of surfactant molecules associate with each of the hydrophobic modifier on a single polymer molecule.

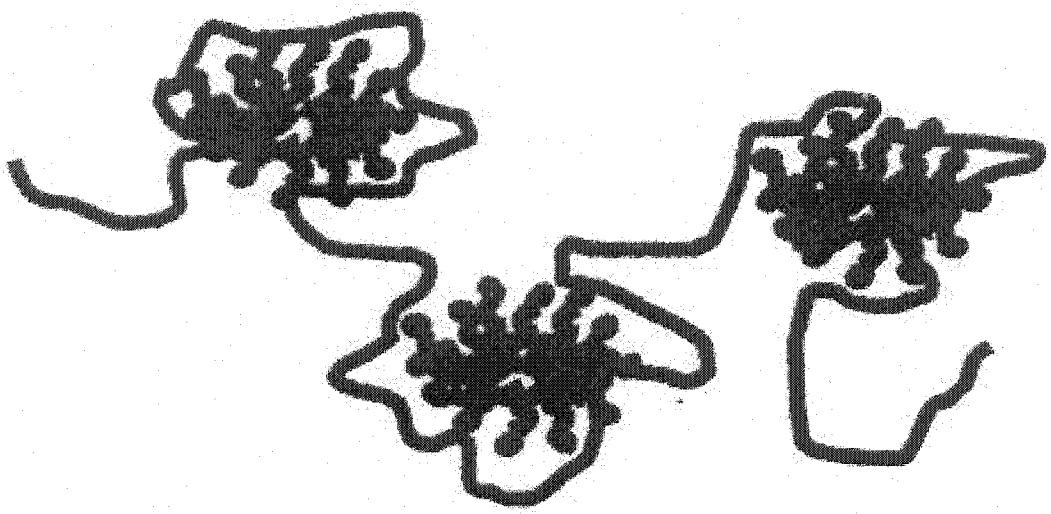


Figure 2.8 Surfactant – polymer structure when the polymer segments partially penetrate and wrap around the polar head group region of the surfactant micelles.

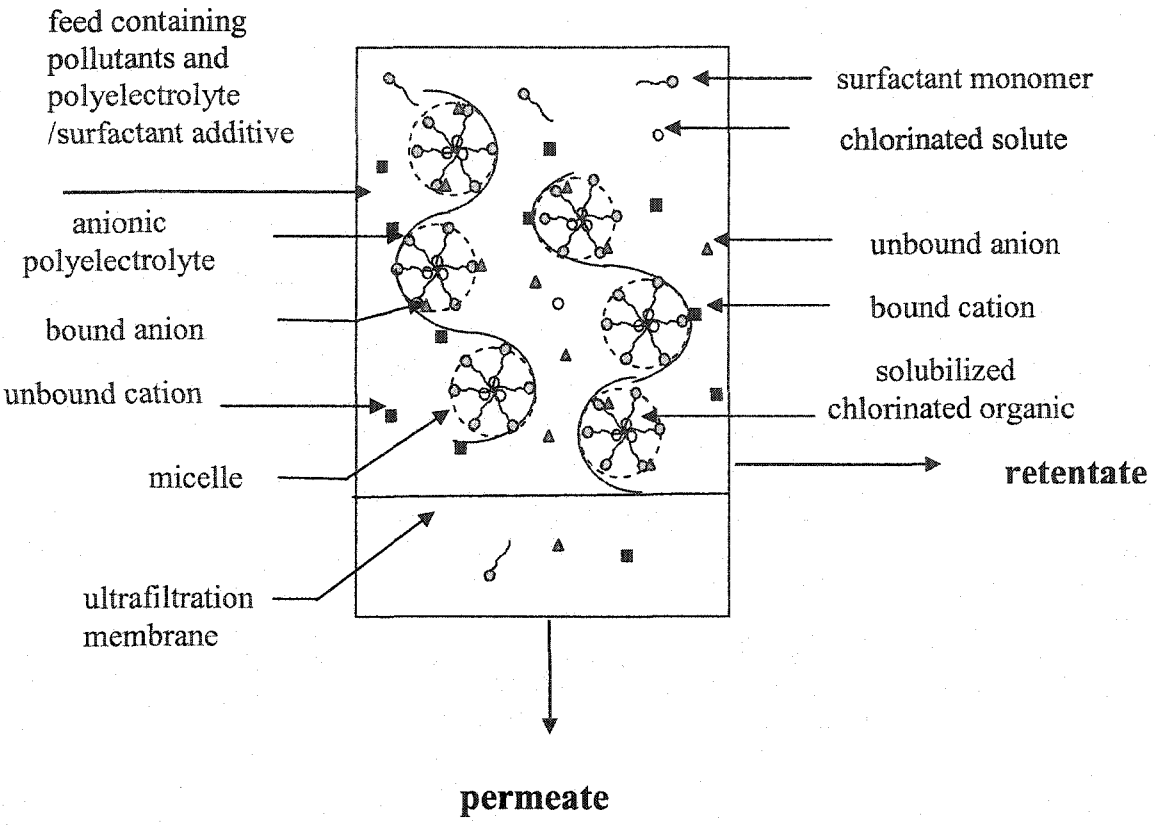


Figure 2.9 Schematic of polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF).

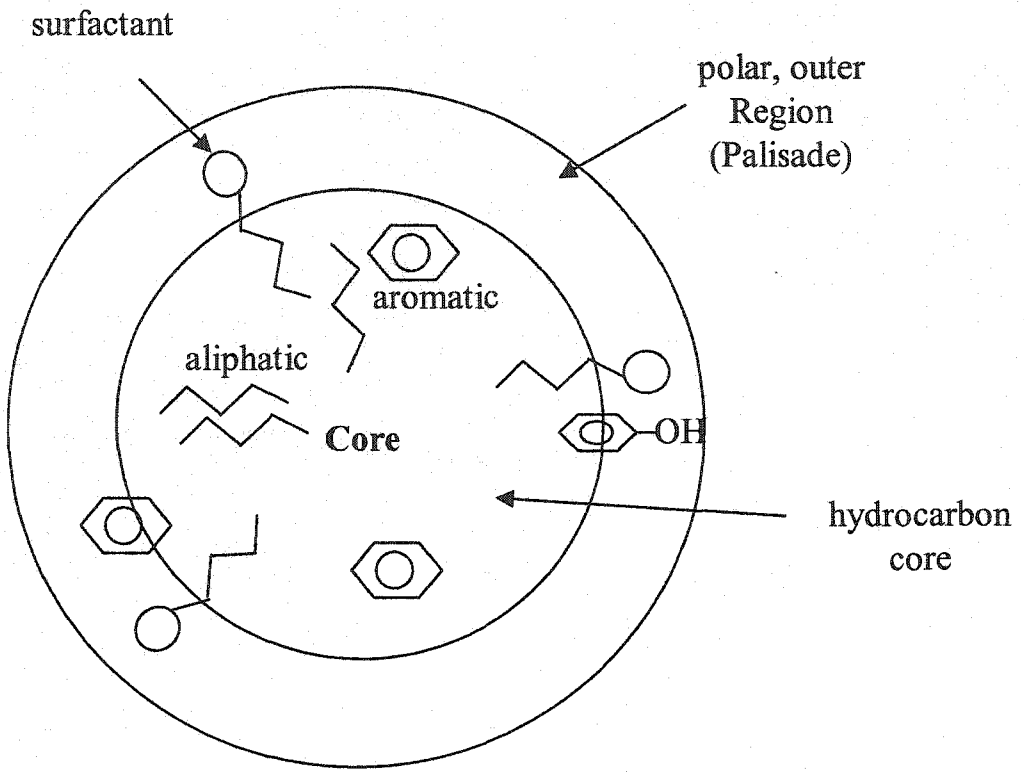


Figure 2.10 Schematic representation of the micellar structure and locus of solubilization of organic solutes in the micelle.

CHAPTER 3

PURIFICATION OF PHENOLIC-LADEN WASTEWATER FROM THE PULP AND PAPER INDUSTRY BY USING COLLOID-ENHANCED ULTRAFILTRATION

3.1 Abstract

The removal of three phenolic pollutants with variable degree of chlorination from water is investigated: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). These compounds are often found in pulp and paper mill wastewater effluent. Colloid-enhanced ultrafiltration (CEUF) techniques are investigated here for this wastewater purification. Pollutants can associate with colloids: surfactant micelles or surfactant - polymer complexes solubilize nonionic compounds. In this application of CEUF, the micelles or surfactant - polymer complexes are ultrafiltered from solution with solubilized chlorinated phenol pollutant. An advantage of surfactant - polymer complexes, compared to only surfactants, is reduction of surfactant monomer (unaggregated surfactant) concentration. These surfactant monomers can pass through the ultrafiltration membrane, reducing the purity of the product water. Excellent solute rejections are observed for both micelles and surfactant - polymer complexes, generally exceeding

90% for DCP and TCP, even exceeding 99% in some cases. The ratio of the solubilization constant in micelles to that in surfactant – polymer complexes varied from approximately 1 to 6. In micelles, rejection increases in the order MCP<DCP<TCP whereas in the surfactant - polymer system, rejection of the DCP and TCP can sometimes reverse order. The surfactant monomer leakage into the permeate for the surfactant - polymer system is only about 1 to 10% of that for the surfactant micelles, down to very low concentrations approaching 1 μM. Therefore, CEUF using surfactant-only or surfactant - polymer mixtures can be a very effective separation technique to remove chlorinated phenols from wastewater. Surfactant - polymer systems result in lower surfactant leakage, but somewhat poorer rejections of the pollutant, and it is anticipated that it will be more difficult to recover the colloid for reuse compared to use of a pure surfactant.

3.2 Introduction

Micelles are surfactant aggregates with the hydrophobic group of the surfactant molecules forming an oil-like interior and the hydrophilic part coating the surface of the micelle[99] (which are roughly spherical for most of the surfactants studied for use in MEUF). Organic solutes can solubilize in different locations in the micelle as mentioned previously. Ionic surfactant micelles can interact electrostatically with highly polar solutes due to strong ion-dipole interaction[112] whereas the hydrophobic core region of the surfactant micelle can interact strongly with hydrocarbon groups of

solutes. As a result, aliphatic hydrocarbons, such as hexane, solubilize primarily within the hydrocarbon core region of micelles. Since chlorine atoms are hydrophobic, for chlorinated phenols, the hydroxyl groups are located next to the cationic surfactant head groups due to ion-dipole interaction while the benzene ring is inserted into the hydrophobic interior of the micelles. In general, the greater the degree of chlorination, the more hydrophobic the solute is and the better it should solubilize[45-46,112,116]. If the solubilized organic molecule has opposite charge to that of the surfactant head groups, solubilization is further enhanced[117]. This can be a factor in this work at pH levels where phenolics can be partially deprotonated and thus anionic.

Not all of the surfactant is present in micelles: the unaggregated individual surfactant is called monomer. The monomer concentration is equal to the critical micelle concentration (CMC) of the surfactant at the solution conditions present. Since the CMC depends on such factors as organic solute concentration, added electrolyte concentration, and temperature, this monomer concentration is not necessarily the same as the CMC value of the pure surfactant at room temperature. In MEUF, the concentration of surfactant in the permeate is approximately equal to the CMC[18-19]. Even for low-CMC surfactants, the monomer leakage can greatly hurt the economics of the separation[22] from the value of the lost surfactant, not even considering potential costs of down stream treatment of the permeate to reduce this surfactant concentration to environmentally acceptable levels.

Several approaches have been tried to address this surfactant leakage problem. The use of ultra-low CMC surfactants invariably involves nonionic surfactants. Unfortunately, fluxes tend to be low (low gel point concentration) with nonionic surfactants[22] due to the lack of electrostatic repulsion between the uncharged micelles in the gel layer. Polymeric surfactants[118-119] should exhibit no monomer leakage, but commercially available ones tend to be predominantly nonionic, with low flux. Another possibility is to treat the permeate with a downstream separation (like foam fractionation)[120-121].

Surfactant - polymer complexes, especially when the polymer and surfactant are oppositely charged, can be in equilibrium with much lower surfactant monomer concentrations than micelles[122], with monomer concentration reductions of two orders of magnitude observed. The surfactant - polymer complexes can solubilize organic solutes with approximately the same level as micelles, per surfactant molecule[45]. Use of these aggregated surfactant - polymer mixtures instead of surfactant alone in the ultrafiltration process is called polymer micellar-enhanced ultrafiltration or PE-MEUF, depicted in Fig. 2.10. It has been shown that surfactant - polymer complexes retain the ability of the surfactant to solubilize hazardous organic solutes, with substantial reduction of surfactant loss through the ultrafiltration membrane[43-45]. Since a higher fraction of the surfactant is in aggregated form, lowering the monomer concentration results in more aggregated surfactant capable of solubilizing solute for surfactant - polymer complexes. However, since surfactant concentrations are generally high in

PE-MEUF or MEUF (most of surfactant in aggregated form), this higher aggregate concentration is a minor factor.

The interaction between ionic surfactants and oppositely charged polymers has been investigated using such techniques as surface tension, dye solubilization, and fluorescence spectroscopy[76,95,122-129]. There have been a few studies of solubilization of organic solutes surfactant - polymer mixtures throughout wide ranges of relative concentrations of organic solutes in the polymer-bound surfactant aggregates, with a partially neutralized copolymer of maleic anhydride and vinyl methyl ether (Gantrez)/cetylpyridinium chloride (CPC) and sodium poly (styrenesulfonate) (PSS)/CPC complexes[43-45]. Since solubilization into the surfactant - polymer aggregate is reported to be similar to that into micelles composed of the same surfactant, the surfactant is deduced to be forming a micellar-like aggregate with a hydrophobic region in which solubilized organic can reside. One potential configuration is "micelles on a string" where the micelles are stabilized by the polymer chain to which they are electrostatically bound[44,76,69,77-78], as depicted in Fig 2.7.

In the present study, the removal of three chloro-substituted phenolics (2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP)) from water using PE-MEUF is compared to removal using MEUF with the same surfactant. The optimum CEUF configuration for the pulp and paper industry wastewater containing chlorinated phenolics is discussed.

3.3 Experimental

3.3.1 Materials

MCP, DCP, and TCP (99+% pure) were obtained from Aldrich Co. (Milwaukee, WI) and used without further purification. High quality (99+% pure) cetylpyridinium chloride (CPC) from Zeeland Chemical (Zeeland, MI) does not exhibit a minimum in a plot of surface tension vs. concentration, or show any impurities in HPLC chromatograms and was used as received. Poly (styrenesulfonate) (PSS) (100% pure), which has an average molecular weight of approximately 70,000 Dalton, was obtained from Alfa Aesar (Ward Hill, MA). The repeating unit of the polymer is $CH_2CH(C_6H_4)SO_3Na$. Lower molecular weight fractions were removed by using a spiral wound ultrafiltration apparatus having 10,000 Daltons molecular weight cut-off and an area of 5 ft^2. The purification process was conducted 5 times. The final concentration of the purified polymer was measured using a Total Organic Carbon analyzer or TOC (Rosemount DC-180). Water was doubly deionized and treated with activated carbon. Sodium hydroxide and hydrochloric acid solutions from Fisher Scientific (Fair Lawn, NJ) were used to adjust the pH of the solutions.

3.3.2 Methods

The semiequilibrium dialysis (SED) method was used to measure solubilization. Regenerated cellulose membranes (6000 Da molecular weight cut-off) were soaked overnight in deionized water prior to mounting them between two compartments. A known volume of a solution containing an organic solute and CPC or CPC - PSS mixtures was placed in the retentate compartment using a 10 mL syringe. The water was placed in the permeate compartment. The cells reached equilibrium within twenty-four hours at 25°C ± 0.1 °C. Each experiment was conducted with two separate SED cells for duplicate points. Osmotic pressure effects caused the water in the permeate to transfer to the retentate; up to a 40% increase in the volume of retentate was observed, especially, at high total colloid (i.e., solute, surfactant, and polymer) concentration. The volume of solution in both compartments was measured using syringes. Concentrations of the chlorinated phenol and CPC in the permeate were determined with a Hewlett-Packard HP 8452A diode array spectrometer. A cuvet with 10-cm pathlength was used to determine solute concentration with minimum detectability of $5x10^{-6}$ M. The concentrations of the chlorinated phenol and CPC remaining in the retentate at equilibrium were inferred by subtracting the analytical concentrations of these species in the permeate from the feed concentration. The pH level of samples was adjusted to 10.5 by using an AR 20 pH/Conductivity meter (Accumet Research, Fisher Scientific) before performing the UV analysis. It should be noted that the pH of calibration solutions was also adjusted to 10.5. Multiwavelength analysis was used to analyze both surfactant and solute concentrations simultaneously. Absorbance values were recorded at different

wavelengths chosen near the absorption maxima of the surfactant and solute (260 nm for CPC, 300 nm for MCP, 314 nm for DCP, and 322 nm for TCP).

Spectrophotometric titrations were carried out to determine the protonation constant (K_H) for the organic solutes in micellar solutions and surfactant – polymer mixtures at room temperature. Spectra were obtained using the spectrometer described previously with a 1 cm pathlength cuvet. Deionized water at several pHs was used to prepare solutions used for the analysis. The pH of the solutions was recorded before performing the UV analysis.

Surface tension measurements, by means of the Wilhelmy plate technique (Kruss Processor Tensiometer K12, Krüss USA, North Carolina), were performed on solutions placed in a crystallizing dish held at constant temperature (25°C ± 0.1 °C). Mixtures of PSS and CPC were prepared and kept at 25°C in a controlled temperature oven overnight. Precipitation was observed at the mole ratios of [CPC]: [PSS] ≥ 1:1; at mole ratios ≤ 1:2, no precipitation was observed and the solutions were isotropic. Only isotropic solutions were used in this study. At some high [CPC] to [PSS] ratios, the solutions would again become isotropic. However, this region was not considered because the beneficial effects of the polymer are not substantial at these surfactant-dominant compositions.

3.4 Theory

The solubilization equilibrium constant (K) of a solute A in CPC micelle or CPC - PSS aggregates is defined as:

$$K = \frac{X_A}{c_A} \tag{3.1}$$

$$X_A = \frac{C_A^{agg}}{C_A^{agg} + C_{CPC}^{agg}} \tag{3.2}$$

where c_A is the concentration of an unsolubilized organic solute, X_A is the mole fraction of the solute (MCP, DCP, or TCP) in the surfactant aggregate, C_A^{agg} is the concentration of solute in the aggregate, and C_{CPC}^{agg} is the concentration of CPC in aggregate form. From material balances:

$$C_A^{agg} = C_{A,tot} - c_A \tag{3.3}$$

$$C_{CPC}^{agg} = C_{CPC,total} - C_{CPC,monomer} \tag{3.4}$$

where $C_{A,tot}$ is the total concentration of the solute in the retentate, c_A is the unsolubilized solute concentration in the retentate (which is essentially the concentration of solute in the permeate compartment), $C_{CPC,total}$ is the total concentration of surfactant in the retentate, $C_{CPC,monomer}$ is the concentration of monomeric surfactant in the retentate. The surfactant concentration in the permeate generally increases to the same concentration as the monomer in the retentate. Then, the permeate surfactant concentration slowly increases as micelles form in the

permeate. Since the permeate micelles could solubilize the solute, the permeate solute concentration is greater than the unsolubilized concentration in the retentate. Therefore, either the equilibration time must be chosen to be short enough so that an insignificant concentration of micelles is formed (although long enough to permit the unsolubilized solute to reach equilibrium), or correction factors used to account for solubilization in permeate micelles[46-49,130]. For PE-MEUF, the polymer is almost completely rejected by the membrane, so it is present in insignificant concentration in the permeate[32], therefore no surfactant – polymer aggregate forms in the permeate. In this study, for micellar systems, we observed 2 orders of magnitude lower concentration of solute and surfactant in the permeate than in the retentate, such that the presence of surfactant micelles in the permeate does not considerably influence the measured solubilization isotherm. Therefore, no correction for permeate micelle formation is made. The distribution of the organic solute and the surfactant in the SED compartments is illustrated in Fig. 3.1.

3.5 Results and Discussion

3.5.1 Effective pKa Values

The phenolic solutes studied here are weak acids and can exist in two protonation states. The unprotonated compound is negatively charged while the protonated phenolics are uncharged. The charged species have higher water solubility

than the neutral, protonated species. The equilibrium or dissociation constant (K_a) of the solutes has been reported in pure water[131]: pK_a = 8.52, 7.9, and 6.0 for MCP, DCP, and TCP, respectively. However, interaction between the phenolic group of the solute and the charged surfactant head groups and charged groups on the polymer, when the solute is solubilized in micelles or surfactant - polymer complexes, can affect the K_a of solubilized species, and therefore, the apparent K_a of the phenolic in the colloid systems.

The equilibrium constant may be evaluated from the protonation step following:

$$L^- + H^+ \underset{}{\overset{K_H}{\rightleftharpoons}} HL \tag{3.5}$$

$$K_H = \frac{[HL]}{[L^-][H^+]} \tag{3.6}$$

where: $[H^+] = 10^{-pH}$

K_H = the protonation constant of the protonation equilibrium (Eq. (3.5))

Values of K_H were obtained by using nonlinear least square program to fit the absorbance-pH data to the following expression[132]:

$$Abs(\lambda) = \frac{Abs_L + Abs_{HL} K_H (10^{-pH})}{1 + K_H (10^{-pH})} \tag{3.7}$$

where: Abs_L = limiting absorbance of basic form of the solute at λ

Abs_{HL}= limiting absorbance of acid form of the solute at λ

$K_H = 1/K_a$

$\log K_H = \log (1/K_a) = pK_a$

All solutions contain the solute of interest at a concentration of 0.2 mM although the actual solute concentration in the SED experiments ranges from 0.5 mM to 25 mM. This is due to the limited range of solute concentration over which the UV spectrum obeys Beer's law when the colloids are also present. Plots of absorbance as a function of pH are shown in Figs. 3.2 through 3.4 for water, 25 mM CPC, and the mixture of 25 mM CPC and 50 mM PSS, respectively. The wavelength selected for each plot is the wavelength where the maximum absorbance (λ_{max}) changes as the pH of the solutions is changed in the presence of 25 mM [CPC]. For example, in the CPC solution at 25 mM, the λ_{max} of MCP, DCP, and TCP is 300, 314, 322 nm, respectively. These values are different from the values observed in pure water; the λ_{max} of the solutes in pure water is 294, 306, and, 312 nm for MCP, DCP, and TCP, respectively. This contributes to the difference in the Abs_L value shown in Figs 3.2 through 3.4. A relatively high Abs_L in the CPC - PSS mixtures is associated with the absorbance of the PSS itself at the chosen wavelength.

Table 3.1 shows the apparent pK_a values obtained from the spectrophotometric titration. The pK_a values in water are close to literature values[131]: 3.28%, 1.1%, and 2.6% different for MCP, DCP, and TCP, respectively. In the micellar solutions, due to the electrostatic interaction between the cationic surfactant and the negatively charged solute, the equilibrium shown in Eq. (3.5) favorably shifts towards the unprotonated form, therefore lowering the apparent pK_a of the solute. On the other hand, in the presence of PSS, the net charge of surfactant - polymer aggregates is negative; the

solute is shifted towards the protonated form, resulting in an increase in the apparent pK_a compared to the pK_a in pure water. By knowing the pK_a values, distribution of species with different charges can be obtained by using software called "Comics"[133], which are shown in Figs 3.5 through 3.7. In micellar solution, the pH of the final retentate solutions ranges from 5.1 to 6.6 for MCP, 5.1 to 6.3 for DCP, and 3.2 to 4.0 for TCP. As shown in Fig. 3.6, the solute is comprised of both neutral form and the negatively charged form, depending on the initial solute concentration. For example, in Fig. 3.6, at the lowest solute concentration for TCP, corresponding to the pH of the final retentate of 4.0, the solution contains 44% neutral form and 56% negatively charged form of TCP. In a similar manner for DCP, at the final pH of 6.3, the solution contains 46% neutral form and 54% negatively charged solute. At the final pH of 6.6 for MCP, the solution contains 70% neutral form and 30% negatively charged solute. It should be noted that the charge distribution was done at a solute concentration of 0.2 mM, with higher solute concentrations, the pK_a can be changed. A series of experiments were carried out at a higher TCP concentration to investigate the effect of solute concentration on the pK_a. At 0.3 mM TCP under the same condition (25 mM CPC), the pK_a slightly shifts to a lower pH (from 3.91 at 0.2 mM TCP to 3.80 at 0.3 mM TCP). The experiment cannot be done at higher solute concentration or in the CPC - PSS mixtures due to the violation of Beer's law that can occur. From this result, it indicates that the percentage of the negatively charged TCP present in the CPC solution can be slightly higher than 56%. In the presence of 50 mM PSS, the pH of the final retentate solutions ranges from 6.6 to 6.7 for MCP, 6.2 to 6.6 for DCP, and

5.3 to 6 for TCP. As shown in Fig. 3.7, the solutes are almost completely protonated or have a slight net negative charge at the pH values studied; the percentage of the phenolate anion is 0%, 0%, and 3% for MCP, DCP, and TCP, respectively.. As mentioned previously, the percentage of the negatively charged solute can be higher than 3% due to the higher solute concentration in the SED experiment higher than in the charge distribution experiment.

3.5.2 Surfactant - polymer Interaction

The PSS concentrations are based on the repeating units, not the total molecular weight. So, for example, 206 g/L of PSS is reported as 1 M based on a repeating unit molecular weight of 206 Daltons even though the total molecular weight is 70,000 Daltons. Fig. 3.8 shows surface tension as a function of CPC concentration at different concentrations of PSS, and Fig. 3.9 is a schematic representation of the curve with generally accepted aggregate structures in each concentration regime[125]. The general features of the surface tension trends in Fig. 3.8 are that there is synergistic lowering of surface tension with increasing PSS concentration below the CPC concentration at which the surface tension reaches a plateau. This plateau surface tension is only mildly dependent on PSS concentration, but is attained at a lower CPC concentration as PSS concentration increases. The PSS can have a massive effect on surface tension lowering. For example, the concentration of CPC required to attain a surface tension of 45 mN/m is approximately 0.7 mM with

no PSS, but only less than 0.002 mM in the presence of 50 mM PSS, which represents over two orders of magnitude reduction. This clearly implies that the PSS is contributing to surface tension lowering and is surface active even in the absence of surfactant as shown in Fig. 3.10. Surfactant - polymer complexes can adsorb at the air -water interface[125], causing the synergistic surface tension lowering observed for the CPC - PSS mixture. However, for purposes of this paper, we are interested in the solution aggregate structure and what these surface tension curves allow us to deduce about the CPC - PSS complexes in solution.

In region a-b-c in Fig. 3.9, surfactant is adsorbing on the polymer chain as unassociated CPC molecules. Lateral interactions between surfactants are negligible since they are at a low adsorption density on the polymer chain. In region c-d, surfactant aggregates which are stabilized by the polymer molecule form "micelles on a string". The concentration of these polymer-stabilized surfactant aggregates in solution increases from c to d. At CPC concentrations above point d, the monomeric CPC concentration increases as the polymer becomes saturated with the surfactant aggregates. At yet higher CPC concentration, eventually ordinary micelles form (point e) and the surface tension tends to plateau again. Goddard has also observed this kind of behavior[125]. Compared to the polymer-free system, this CPC concentration required to form micelles is much higher because a vast majority of surfactant is present in surfactant - polymer complexes instead of monomer when this micelle formation concentration is attained. This CPC concentration was not reached for any of the PSS concentrations studied in Figure 3.8, primarily because the polymer

and surfactant form a precipitate prior to this concentration. It should be noted that this type of behavior has also been observed in a turbidity plot versus concentration of a surfactant[134].

It is the surfactant aggregate, stabilized by polymer, which is solubilizing the organic pollutant in PE-MEUF, so the CPC concentration needs to be above point c. However, in the PE-MEUF, at a total CPC concentration above point e, the CPC monomer concentration would be equal to the CMC, and the surfactant permeate concentration reduction advantage of the PE-MEUF would be lost. The higher the PSS concentration, the lower the CPC concentration at which the polymer-stabilized surfactant aggregate forms (point c). It was observed that the gel point (colloid concentration in retentate where flux becomes zero) in the 1:2 surfactant - polymer complex solution is approximately 0.4 M in CPC concentration[44], corresponding to 0.8 M in PSS concentration. In the case of the surfactant-only solution, the gel point is 0.53 M (19) whereas the gel point is approximately 0.7 M in the polymer-only system[135]. The total colloid (surfactant plus polymer) concentration in the PE-MEUF is higher than the colloid concentration when either the surfactant or polymer is present alone, but the surfactant concentration at the gel point is less for PE-MEUF than for MEUF. At lower [CPC] to [PSS] ratios, a lower surfactant concentration is present at the gel point. Therefore, [CPC] to [PSS] ratio in the retentate is a compromise between a higher fraction of surfactant in aggregated form at a low [CPC] to [PSS] ratio, but a reduced ability to increase the retentate surfactant concentration until unacceptably low fluxes are observed. The latter translates to lower

permeate/feed or water recycle ratios. So the information in Fig. 3.8 can help determine the optimum polymer and surfactant feed concentrations in PE-MEUF. It is important to note that since the PSS concentration affects the surface tension at a given CPC monomer concentration, one cannot deduce CPC monomer concentration from the value of surface tension. Therefore, we will show permeate CPC concentrations which approximate this CPC monomer concentration in the retentate.

From the data in Fig. 3.8, and referring to Fig. 3.9, point d corresponds approximately to a CPC - PSS molar ratio of 1/2, so two anionic sulfonate PSS groups stabilize one aggregated cationic surfactant molecule. Previous studies[44] in our group indicated that at a [CPC]/[PSS] ratio of 1/2 or less, there is no precipitation of the surfactant - polymer mixture. At a [CPC] to [PSS] ratio greater than about 1, some precipitation will occur and redissolution may be slow. Thus, [CPC] to [PSS] ratios of 1 to 3 and 1 to 2 were used in SED experiments in this work.

3.5.3 Solubilization Isotherms

As shown in Figs. 3.11 through 3.16, the solubilization equilibrium constants obtained by SED experiments for 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6- trichlorophenol (TCP) are plotted as a function of intramicellar mole fraction (X_A) in CPC micelles and CPC - PSS complexes. From Figs. 3.11 through 3.13, solubilization capacity in a surfactant - polymer system is lower than that in a polymer-free system. Depending on the solute type and concentration, as the solute concentration increases, the ratio of the solubilization constant in micelles to

that in surfactant - polymer complexes varies from 1.5 to 2.5 for MCP, from 1 to 1.6 for DCP, and from 2.2 to 4.9 for TCP. The solubilization constant decreases monotonically with increasing X_A for CPC-only, and for CPC - PSS complexes at higher values of X_A. Unlike the micellar systems, K exhibits a slight maximum with X_A for MCP and TCP in surfactant - polymer systems. The polymer causes the greatest reduction in K for TCP, compared to MCP and DCP. The reduction in K caused by the polymer is the greatest at low solute concentrations. In addition, compared to CPC system, the solubilization ability of CPC - PSS complexes is less dependent on the solute concentration (or X_A), particularly for MCP.

The data is replotted in Figs. 3.14 through 3.16 to show the effect of solute structure. In the polymer-free system, shown in Fig. 3.14, the solubilization constant (K) has the order $K_{MCP} < K_{DCP} < K_{TCP}$, and K monotonically decreases as X_A increases for MCP, DCP, and TCP. In the surfactant - polymer systems, shown in Figs. 3.15 and 3.16, $K_{TCP} < K_{DCP}$ at $X_A < 0.25$; but $K_{DCP} < K_{TCP}$ at $X_A > 0.25$, whereas K_{MCP} is less than K_{DCP} or K_{TCP} over the entire concentration range. At both [CPC] to [PSS] ratios of 1 to 2 and 1 to 3, K_{TCP} has a maxima near $X_A = 0.2$.

Differences in solubilization behavior of the solutes in CPC micelles and in CPC - PSS complexes may be attributed to a reduction in electrostatic inter-headgroup interaction upon the formation of the smaller polymer-stabilized micelles, resulting in a reduction in both CMC and surfactant aggregation number[127] and presumably electrical potential at the surface of surfactant aggregates. Therefore, solutes partition more strongly into the ordinary micelles compared to the surfactant - polymer

aggregates for all three solutes, probably due to increased ion-dipole interaction between the cationic surfactant headgroup and the phenolic solute hydroxyl group. The neutralization or partial neutralization of surfactant aggregates by the oppositely charged polymer would be expected to have a greater effect on solubilization of more acidic solutes than the less acidic solutes. It should be noted that the pK_a of DCP is higher than MCP in the CPC - PSS mixtures (at 1/2 mole ratio), as shown in Table 3.1 although the pK_a of DCP is more than MCP in both water and CPC solutions. As predicted from pK_a values, the highest ratio of K for CPC to K for CPC - PSS is observed for TCP, and the lowest ratio of the K values is found for DCP. However, as the solute concentration approaches zero, the effect of polymer is relatively large; a greater reduction in K is observed for DCP than for MCP. This behavior was also observed in CPC/Gantrez mixtures[45]. It should also be noted here that the [CPC] to [PSS] ratio does not significantly influence the solubilization of the solutes at the same surfactant concentration for the 1 to 2 and 1 to 3 ratios studied here.

Hydrophobicity of the solute has been considered to be a key factor in dictating solubilization behavior although other factors, such as polarizability and substitution site, are also important. In general, the more hydrophobic the solute, or the lower the water solubility, the higher the solubilization constant. It should be noted that the water solubility of 2-MCP, 2,4-DCP, and 2,4,6-TCP are 2, 0.4, and 0.04 wt.% (or 0.173, 0.034, and 0.002 M), respectively[136]. The value of K for the three solutes is in inverse order compared to water solubility for the surfactant-only system as seen in Fig. 3.14. For instance, K_{TCP} to K_{DCP} ratio is ranging from 2 to 3.4, while the water

solubility ratio for DCP to TCP is 17. In addition, as mentioned previously, a higher percentage of the negatively charged solute was observed in TCP than MCP or DCP at low solute concentration, therefore increasing the K value of TCP as compared to the K value of DCP or MCP.

In general, a decrease in the solubilization equilibrium with an increasing mole fraction has been observed in micelles for alcohols and other polar solutes[137]; as shown in Fig. 3.14, we observed this trend here for CPC with all three solutes. At low concentrations, K can vary linearly with solute concentration in the micelles, so that

$$K = K_0(1 - bX_A) \tag{3.8}$$

where K_0 is the value of the solubilization constant in the limit as X_A approaches zero. Dougherty and Berg have been found a linear dependence of K vs. X_A at low solute concentration for several surfactant-polar organic solute systems[138]. By inserting the definition of K [Eq. (3.1)] and rearranging Eq. (3.8), the resultant equation yields a Langmuir adsorption isotherm.

$$X_A = \frac{K_0 c_A}{1 + K_0 b c_A} \tag{3.9}$$

This behavior suggests that the solute is initially located at the micellar surface at low X_A. Once all active sites are occupied, the solubilization may occur deeper into the palisade region or into the hydrocarbon interior of the micelles as supported by an upward curvature in the plot of K vs. X observed in both MCP and DCP which implies an increase in micellar solubility at high occupation number. This means that the Langmuir isotherm fails at higher MCP, DCP, and TCP concentrations. It is plausible that the solutes penetrate deeper into the palisade layer or are incorporated

into the hydrocarbon interior of micelles by hydrophobic interaction between the chloro group of the solute and the hydrocarbon core of the micelle.

Previous studies[46,47] have shown the linear correlation of $\sqrt{K}$ against X_A over the entire range of solute concentration. Our solubilization results also fit the correlation of $\sqrt{K}$ vs. X_A better than a linear plot of K vs. X_A. However, $\sqrt{K}$ vs. X_A did not produce an excellent correlation and does not have a strong theoretical basis, so is not used here.

Since the solutes are almost completely protonated under the conditions in the presence of polymer, ion-dipole interaction can affect the solubilization of the solute in the surfactant aggregate. The dipole moment (μ) of MCP, DCP, and TCP is reported as 2.93, 2.25, and 1.08 D, respectively[139], which has an opposite order to hydrophobicity of the solute (e.g., TCP shows the greatest hydrophobicity). As a result, two opposing effects for a given solute are viewed here; a solute with higher degree of chlorination like TCP with the highest hydrophobicity is speculated to have the lowest ion-dipole interaction. This effect can presumably explain the results for DCP and TCP, shown in Figs. 3.15 and 3.16. At low solute concentrations, the ion-dipole interaction between the solute and the surfactant - polymer aggregate plays a greater role than the effect of hydrophobicity; therefore, at a given solute concentration, a higher K value is observed in DCP than TCP. However, at higher solute concentration, besides the effect of the hydrophobicity, TCP may be solubilized more deeply into the core of the micelle as mentioned previously; as a result, the solubilization constant of TCP is higher than that of DCP. The solubilization of MCP

in both figures are smallest over an entire range of concentration because of its lower hydrophobicity, and higher water solubility, compared to DCP and TCP, although its dipole moment is the highest.

3.5.4 Solute Rejection

Solute rejection is a more convenient parameter than the solubilization equilibrium constant to use in process design for the UF processes, and it is defined in Eq. (2.4). At high rejections (as rejection approaches 100%), rejection values are not sensitive to separation efficiency. Permeate to retentate solute concentration ratios of 1 to 10, 1 to 100, and 1 to 1000 correspond to rejection of 90%, 99%, and 99.9%, respectively. A typical retentate solute to colloid concentration ratio in CEUF is 1 to 10: Table 3.2 shows the rejection values at this condition for MCP, DCP, and TCP for MEUF and PE-MEUF. The experiments were performed at constant colloid concentrations of 25 mM, 75 mM, and 100 mM for the CPC only system, a [CPC] to [PSS] ratio of 1 to 2, and a [CPC] to [PSS] ratio of 1 to 3, respectively, while retentate solute concentration was varied. Therefore, corresponding to the ([solute] to [colloid])$_{ret}$ ratio of 1 to 10, [solute]$_{ret}$ for the colloid concentrations of 25 mM, 75 mM, and 100 mM are 2.5 mM, 7.5 mM, and 10 mM, respectively.

If a pollutant permeate concentration is unacceptably high, the feed colloid concentration can be increased and/or the process can be staged. For example, in a previous study, about four stages were found to be optimum for removal of 99% of

trichloroethylene from groundwater[140]. Rejections below 80% could be considered not very efficient, above 95% good and above 98% excellent as rough guides. So, from Table 3.2, use of MEUF for removal of MCP is feasible, but use of PE-MEUF for MCP does not appear promising if substantial concentration reductions are required. Nonetheless, the removal of DCP and TCP can be accomplished by use of both MEUF and PE-MEUF; the rejections of DCP and TCP exceed 95%. In, PE-MEUF systems, an increased colloid concentration from 75 mM to 100 mM does not significantly influence the DCP and TCP rejections because, although, the colloid concentration is increased, the retentate solute concentration is increased as well.

3.5.5 Surfactant Leakage

As shown in Figs. 3.17 through 3.22, the surfactant (CPC) concentration in the permeate or "surfactant leakage", studied with MCP, DCP, and TCP, in the MEUF and PE-MEUF systems, are plotted as a function of retentate solute concentration. As seen in Figs. 3.17 through 3.19, the extent of surfactant leakage can be reduced by as much as approximately 2 orders of magnitude due to the presence of PSS; the retentate [CPC] to [PSS] ratio of 1 to 2 gives a slightly lower extent of the surfactant leakage than does a ratio of 1 to 3. The data is replotted in Figs. 3.20 through 3.23 to show the effect of solute structure.

For PSS-free systems, the CMC can be deduced from the surface tension data (see Fig. 3.8). With varying the solute type and concentration, the CMC results for

MCP and DCP are shown in Fig. 3.24. The effect of TCP is not shown here because of its very limited solubility below the CMC. A significant reduction in the CMC due to solubilization of solutes is observed (approaching an order of magnitude) with a greater CMC depression at higher unsolubilized solute concentrations. This effect is due to reduction in repulsion between the positively charged surfactant head groups upon insertion of the phenolic hydroxyl groups between them (reduction in electrical potential at micelle surface). Ion-dipole interactions between surfactant head groups and solute hydroxyl groups also help stabilize micelles and reduce the CMC. At a given unsolubilized solute concentration (c_A), DCP has a higher K value and so, higher X_A [Eq. (3.1)], so the greater effect of DCP than MCP on CMC depression shown in Fig. 24 at a given unsolubilized solute concentration is expected.

When the surfactant concentration is at the CMC, all of solute in solution is unsolubilized and the monomer concentration equals the CMC. When the total surfactant concentration is above the CMC and some of the solute is solubilized, the surfactant monomer concentration is equal to the CMC at a solute concentration (from Fig. 3.24) which is equal to the unsolubilized solute concentration (c_A) in the retentate solution, not the total solute concentration in the retentate. Therefore, when permeate surfactant concentrations are compared to that of the monomer in the retentate (for PSS-free systems), it is this CMC which is used to estimate the equilibrium monomer concentration. The retentate monomer concentration [deduced from its CMC values (Fig. 3.24) at a given unsolubilized solute concentration] is shown as an additional curve in Figs. 3.17 and 3.18 for MCP and DCP, respectively.

As shown in Figs. 3.17 through 3.18, for MEUF, the surfactant leakage (CPC concentration in permeate) for MCP and DCP is approximately 20% higher than its CMC values. In the micellar systems studied here, it is observed that the equilibrium $[CPC]_{ret}$ is approximately 5% different from initial $[CPC]_{ret}$. Therefore, the assumption that solubilization is insignificant in the permeate is justified. At a given solute concentration, the surfactant leakage is in the order of TCP<DCP<MCP, as shown in Fig. 3.20. This effect is due to the increased solubilization and decreased monomer concentration with increasing hydrophobicity of the solute (Figs. 3.14 and 3.24). In Fig. 3.23, the surfactant leakage is shown as a function of X_A and, in general, minimum surfactant leakage is seen for TCP, followed by DCP, then MCP. This indicates that at a given degree of solubilization (X_A), the greater reduction of head group repulsion for the more hydrophobic solute results in a slightly lower surfactant monomer concentration in the retentate and lower surfactant leakage. However, it is the dramatic effect of solute structure on K (Fig. 3.14) which is the main cause of degree of chlorination of the solute on surfactant leakage.

As shown in Figs. 3.17 through 3.19, the surfactant leakage in MEUF systems relative to that in PE-MEUF systems ($[CPC]_{perm,MEUF}/[CPC]_{perm,PE-MEUF}$), decreases with increasing retentate solute concentration; the ratio ranges from 4 to 46.7 for MCP, 5.5 to 86.7 for DCP, and 2.5 to 120 for TCP. In other words, in the PE-MEUF systems, the surfactant leakage increases with increasing solute concentration in the retentate. This effect is presumably due to further solubilization of the solute reducing surfactant - polymer interaction or stabilization, resulting in an increase in surfactant

monomer concentration. An increased PSS concentration (or increased colloid concentration) slightly enhances the surfactant leakage; as is obvious in the system studied with TCP. This is probably due to an increased ionic strength, resulting in an increase in the critical aggregate concentration (48), thus an increase in surfactant monomer concentration in the retentate.

Comparing the surfactant leakage to that at equilibrium, as seen in Fig. 3.8, at a [PSS] of 50 mM, surface tension reaches the plateau region at point c which approximately corresponds to a [CPC] of 0.006 mM. An increase in [CPC] up to point d in Fig. 3.9 does not significantly change the unaggregated surfactant concentration because the additional surfactant forms aggregates with the polymer. As a result, at a given [PSS], surfactant monomer concentration can be estimated from the surfactant concentration at point c, which is approximately 0.006 mM for 50 mM PSS concentration. However, there is no organic solute present in this case. In the presence of solute, the solubilization of solute in the surfactant - polymer aggregates can increase the surfactant leakage as just discussed. The extent of the surfactant leakage, in the presence of 50 mM PSS, increases from about 0.05 to 0.13 mM for MCP, 0.01 to 0.1 mM for MCP, and 0.005 to 0.02 mM for TCP mM with increasing retentate solute concentration. The lower range of this surfactant leakage (when the solute is infinitely dilute) is relatively close to the monomeric CPC concentration at equilibrium from Fig. 3.8. Therefore, the permeate surfactant concentrations can be approximated by the equilibrium surfactant monomer concentration in the retentate for both MEUF and PE-MEUF. However, it is important to note that the cac cannot be correctly

interpreted as the concentration of free surfactant at the onset of surfactant - polymer aggregate formation since a fraction of the surfactant molecules would be bound to the polyions when the cac is attained.

As shown in Figs. 3.21 and 3.22, maximum surfactant leakage is observed for MCP, compared to DCP and TCP. In the absence of PSS, the higher degree of chlorination causes greater CMC depression as shown in Fig. 3.24. Although the CMC values in the presence of TCP are not available, we presume that TCP would cause even greater depression at a given solute concentration. Like the polymer-free system, it is reasonable to expect the same qualitative effect of the type of solute on the surfactant - polymer systems (Fig. 3.21); for example, MCP shows greater surfactant leakage than DCP and TCP

Table 3. 1 pKa values of MCP, DCP, and TCP in water, CPC solutions, and CPC - PSS mixtures.

solute	MCP	DCP	TCP
Water	8.80	7.99	6.16
CPC (25 mM)	6.98	6.22	3.91
CPC - PSS (25 mM/50 mM)	9.09	9.54	7.52

Table 3. 2 Rejection of solute at [solute] to [colloid] = 1 to 10.

[CPC - PSS]	25 mM/0	25 mM/50 mM	25 mM/75 mM
MCP	85.0%	76.0%	70.0%
DCP	97.3%	95.5%	95.0%
TCP	99.0%	96.3%	95.5%

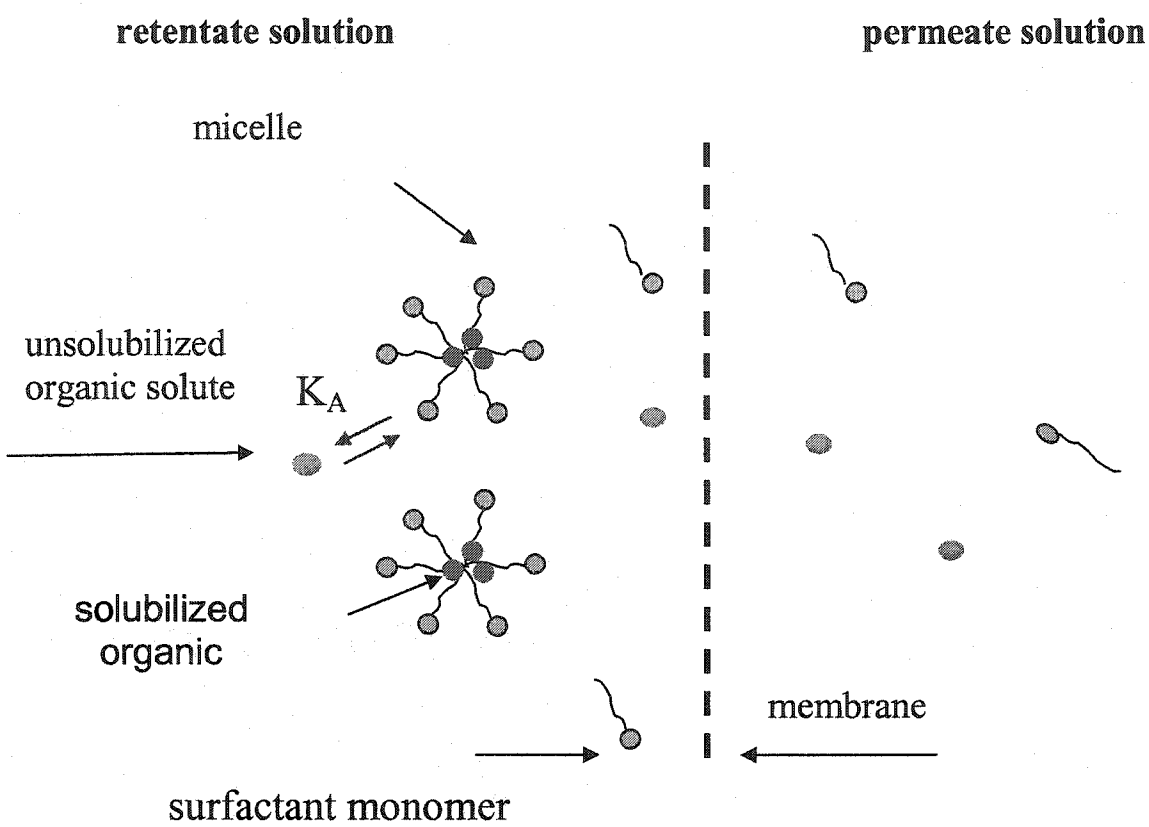


Figure 3. 1 Distribution of surfactant and organic solute in SED compartments.

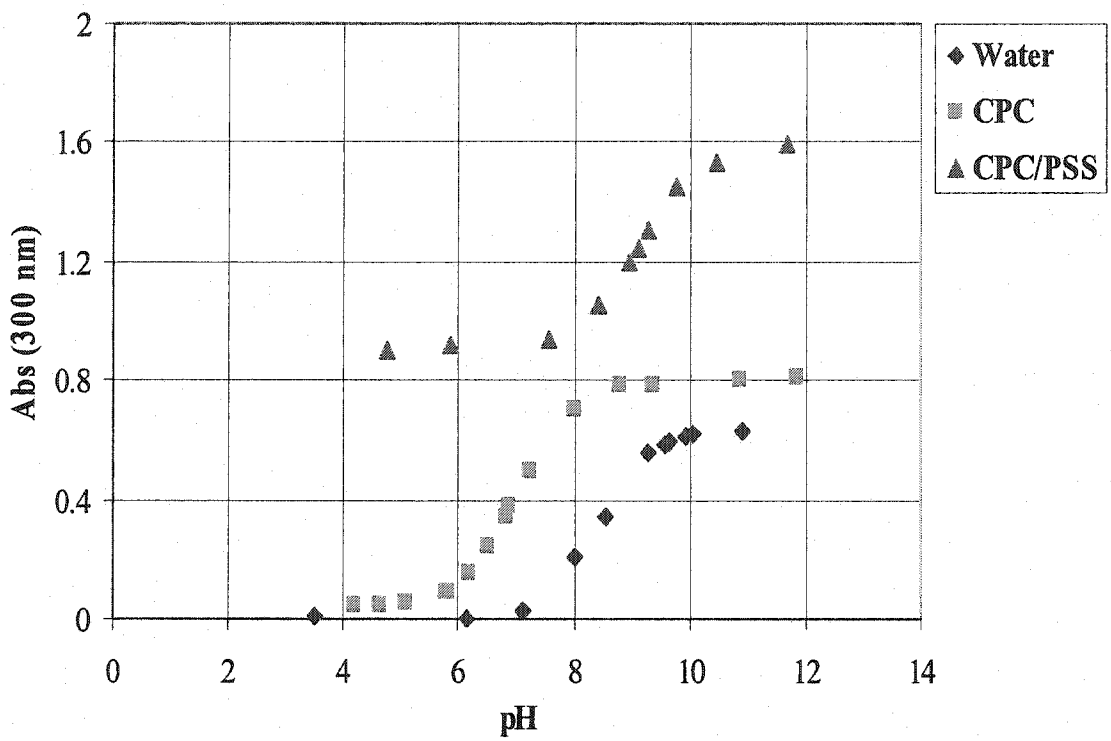


Figure 3. 2 Plots of pH versus absorbance at 300 nm for MCP in water, 25 mM CPC, and the mixture of 25 mM CPC and 50 mM PSS.

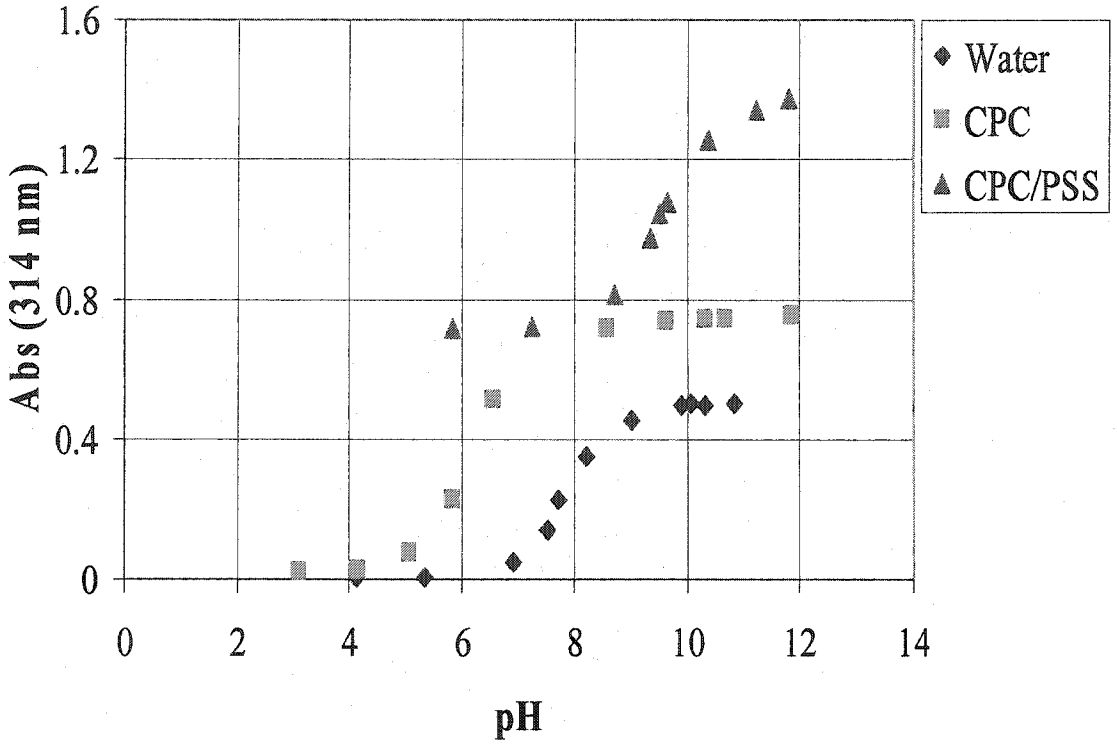


Figure 3. 3 Plots of pH versus absorbance at 314 nm for DCP in water, 25 mM CPC, and the mixture of 25 mM CPC and 50 mM PSS.

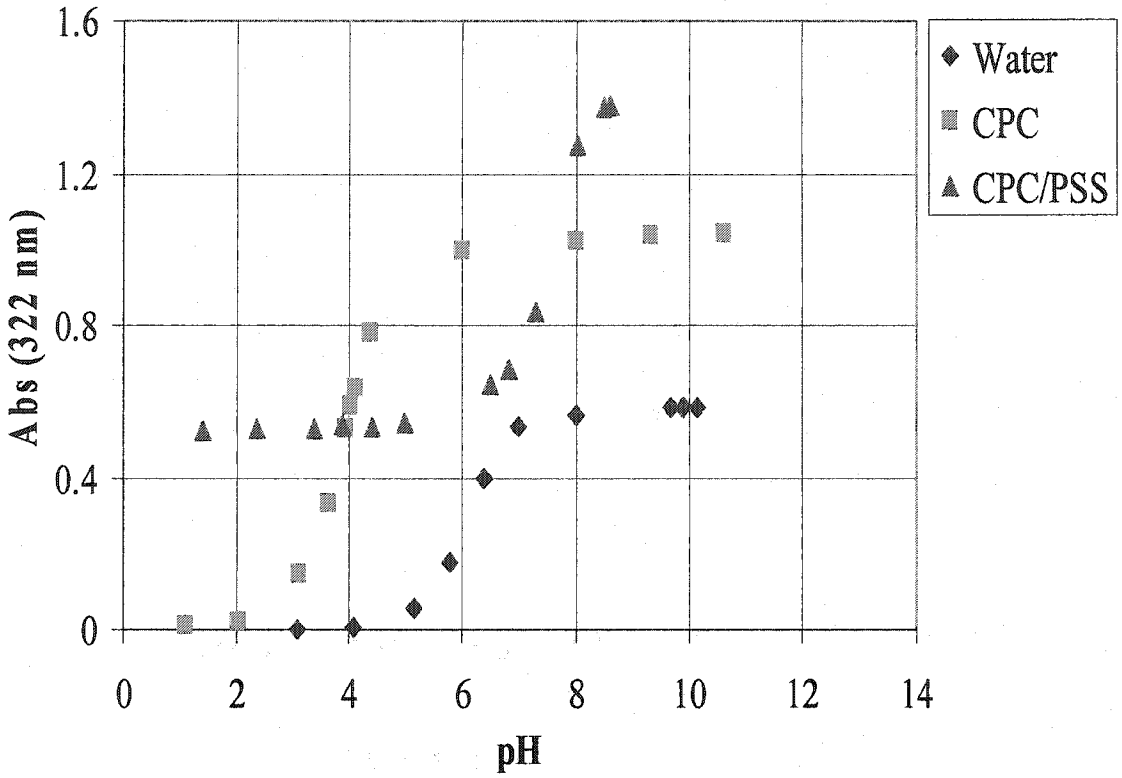
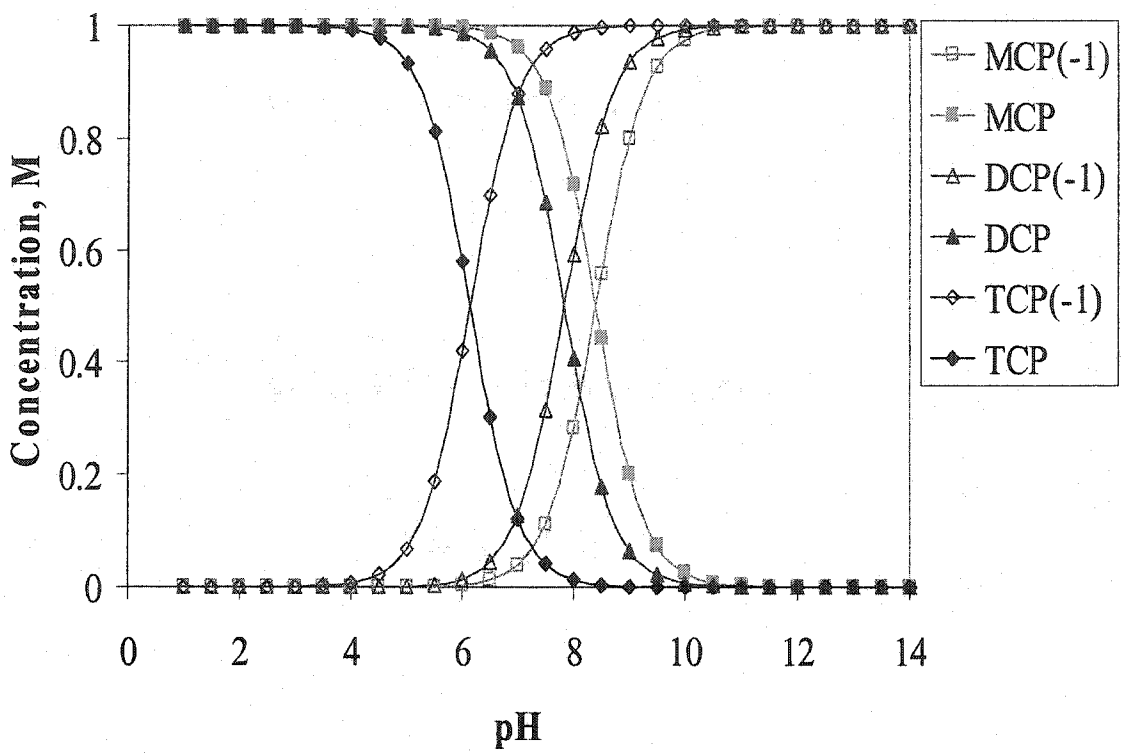
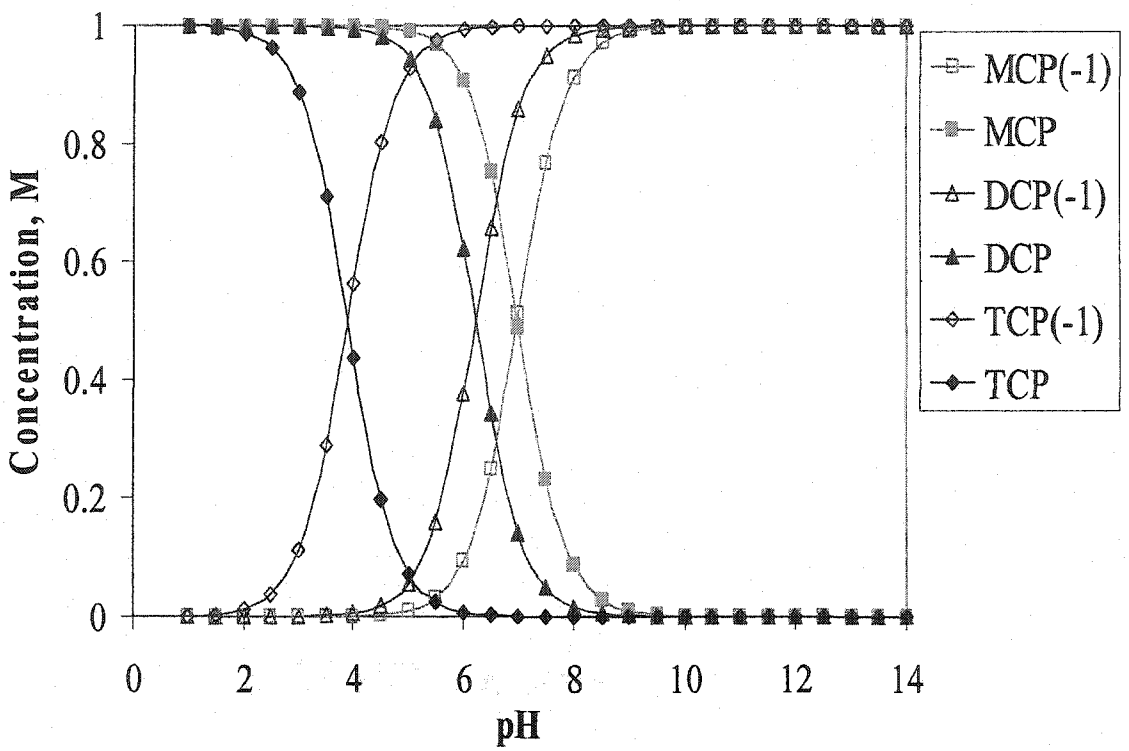


Figure 3. 4 Plots of pH versus absorbance at 322 nm for TCP in water, 25 mM CPC, and the mixture of 25 mM CPC and 50 mM PSS.



(-1) represents the negatively charged species

Figure 3. 5 Charge distribution of MCP, DCP, and TCP in water.



(-1) represents the negatively charged species

Figure 3. 6 Charge distribution of MCP, DCP, and TCP in 25 mM CPC.

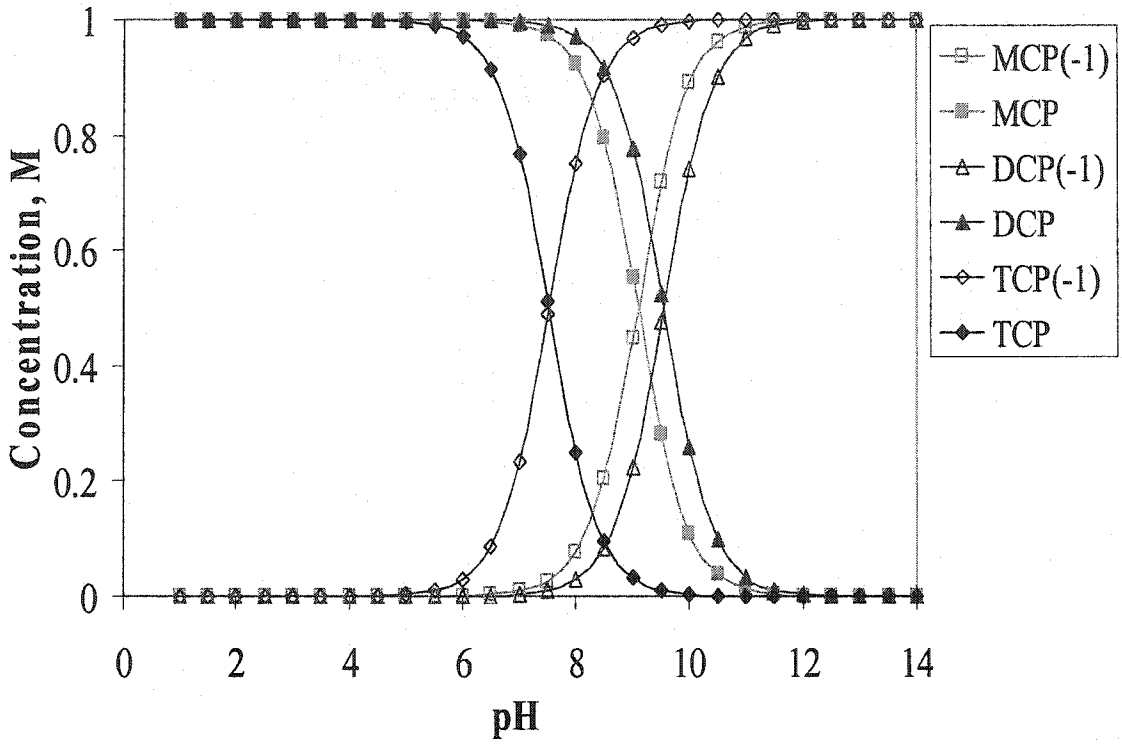


Figure 3. 7 Charge distribution of MCP, DCP, and TCP in the mixture of 25 mM CPC and 50 mM PSS.

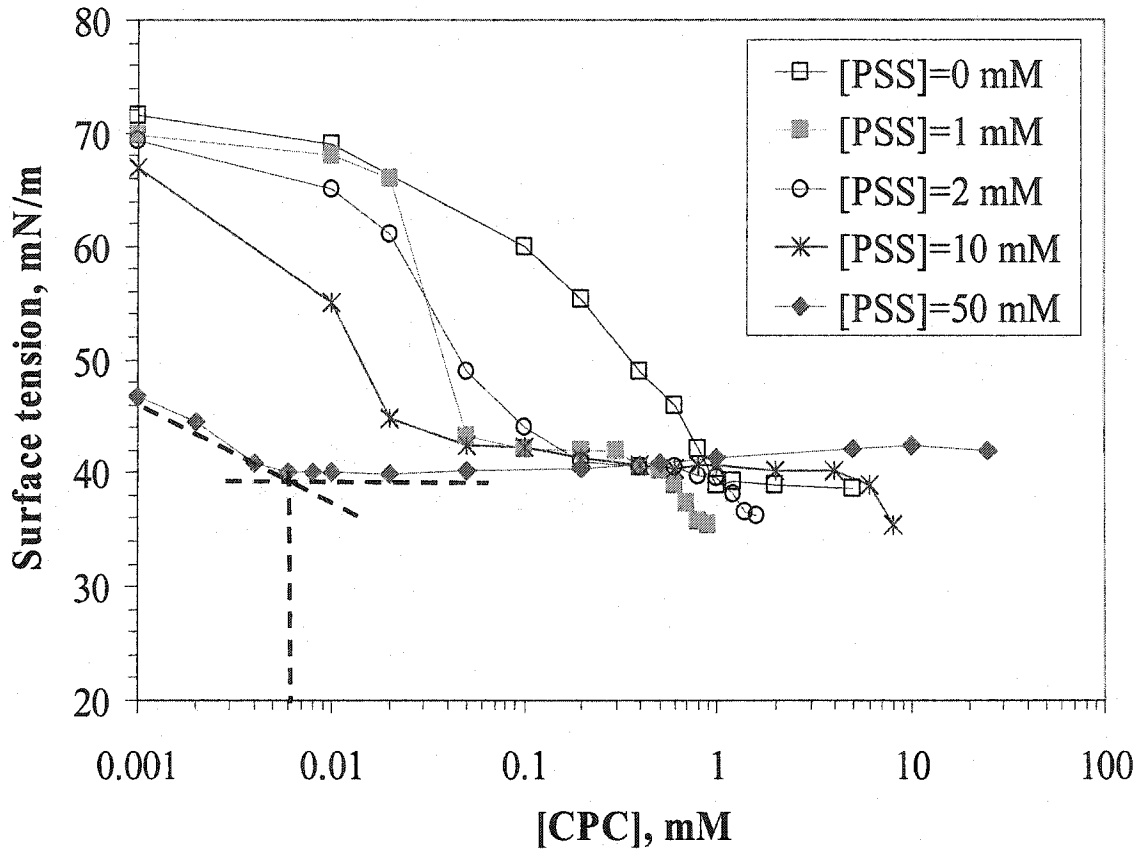


Figure 3. 8 Surface tension of surfactant and surfactant - polymer systems.

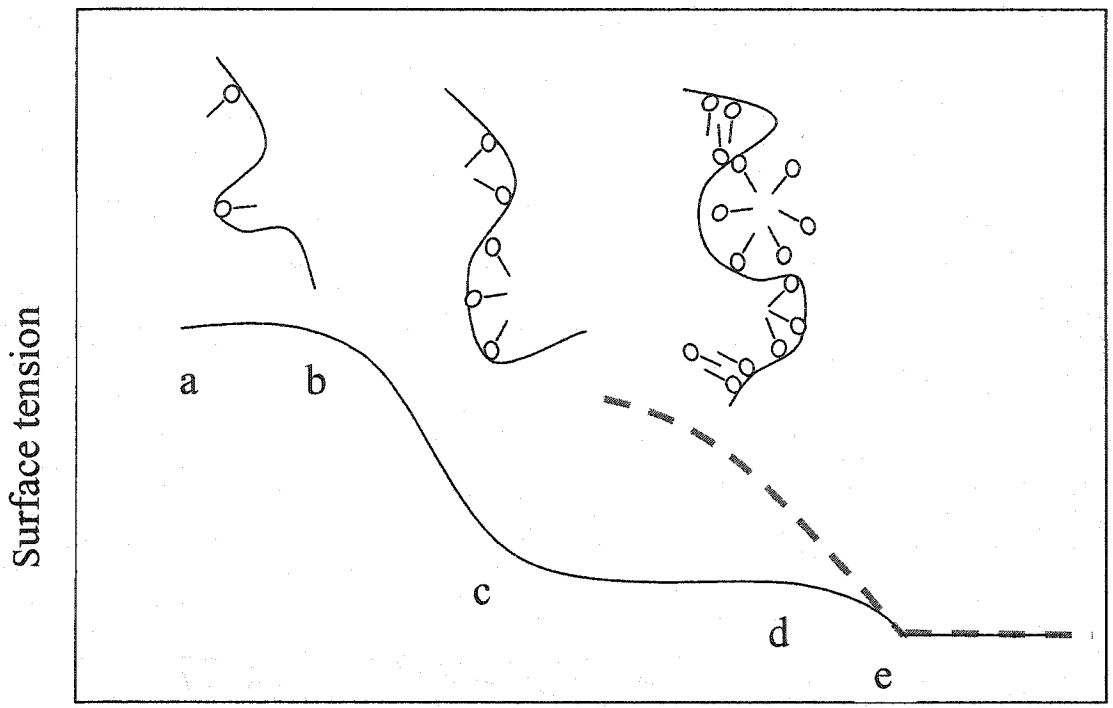


Figure 3. 9 A schematic of surfactant - polymer aggregation. Dashed line is for the surfactant (CPC) alone. Full line is for CPC - PSS mixture. Counterions are not depicted here.

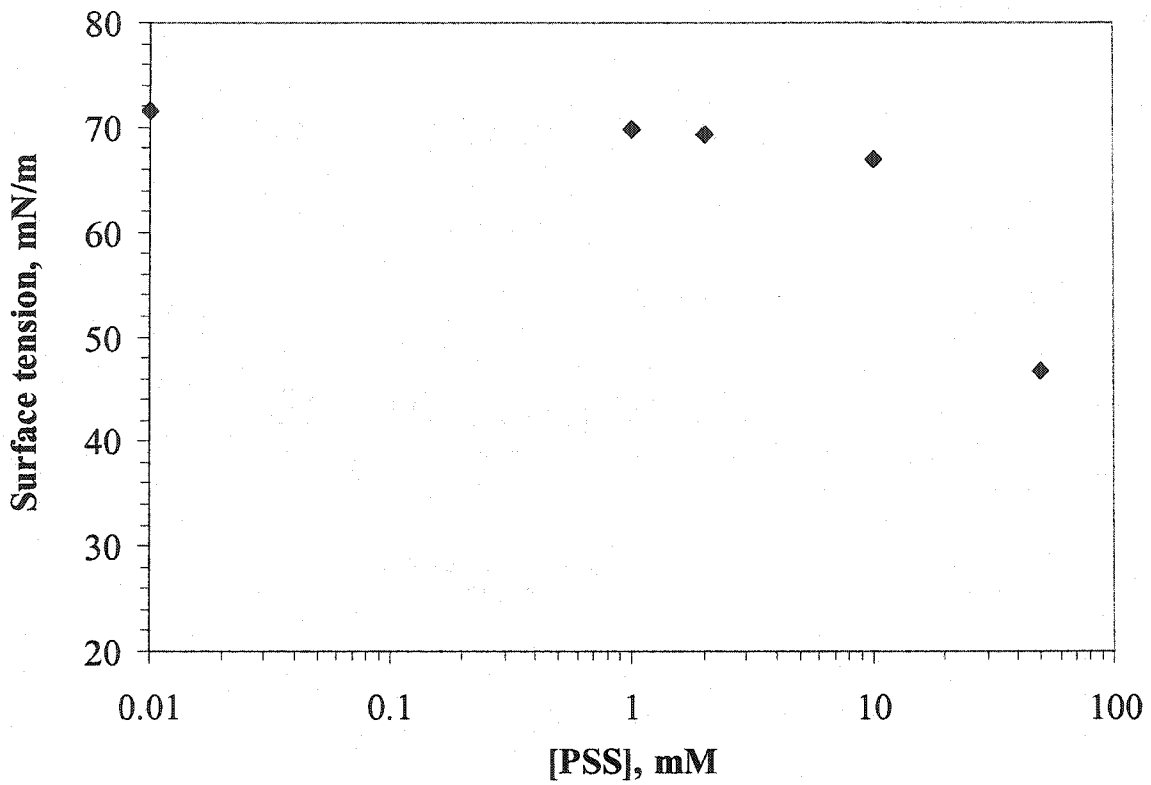


Figure 3. 10 Surface tension for PSS-only solutions.

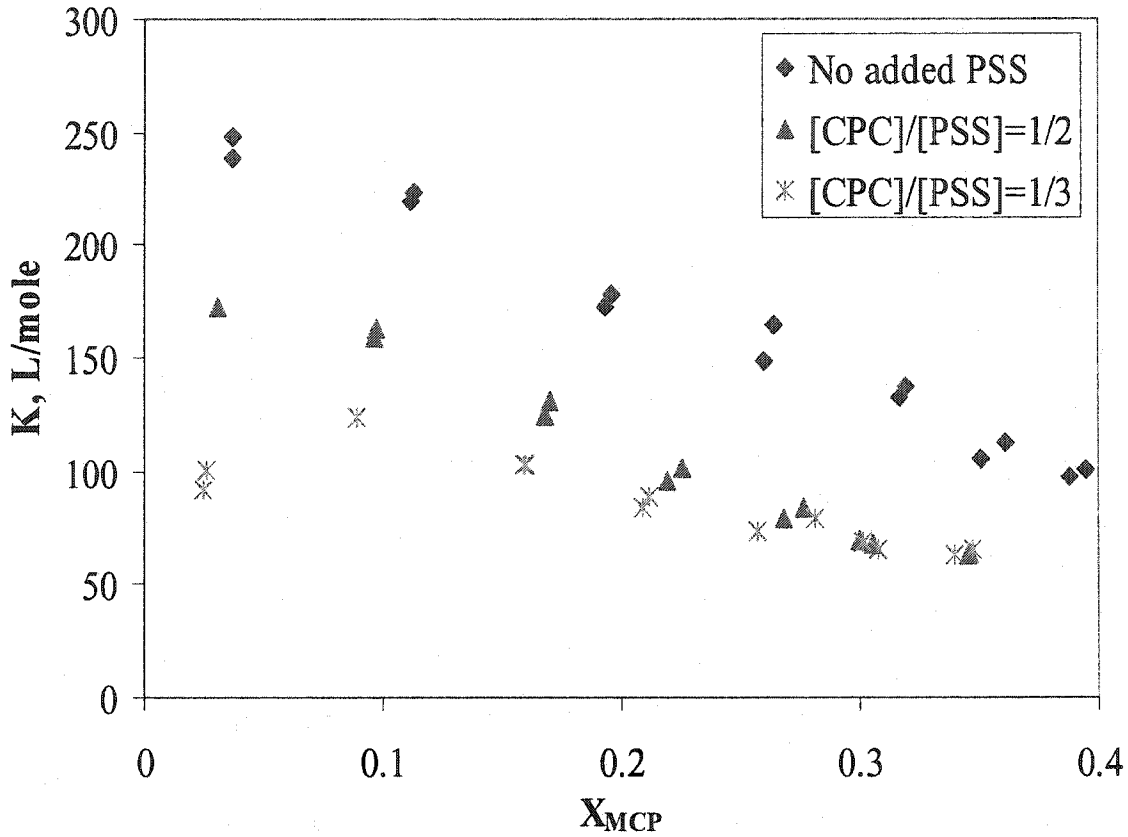


Figure 3. 11 Solubilization equilibrium constant of MCP vs. mole fraction of MCP in the micelle, with and without PSS. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

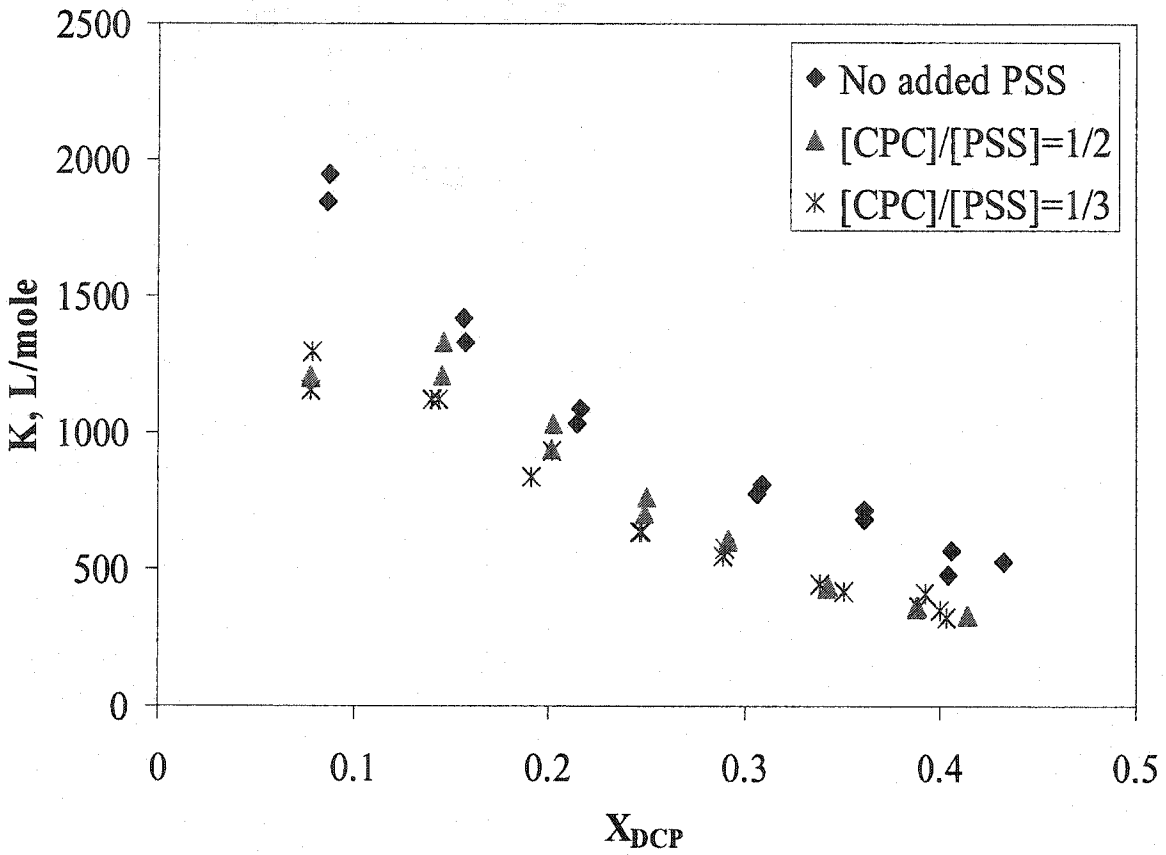


Figure 3. 12 Solubilization equilibrium constant of DCP vs. mole fraction of DCP in the micelle, with and without PSS. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

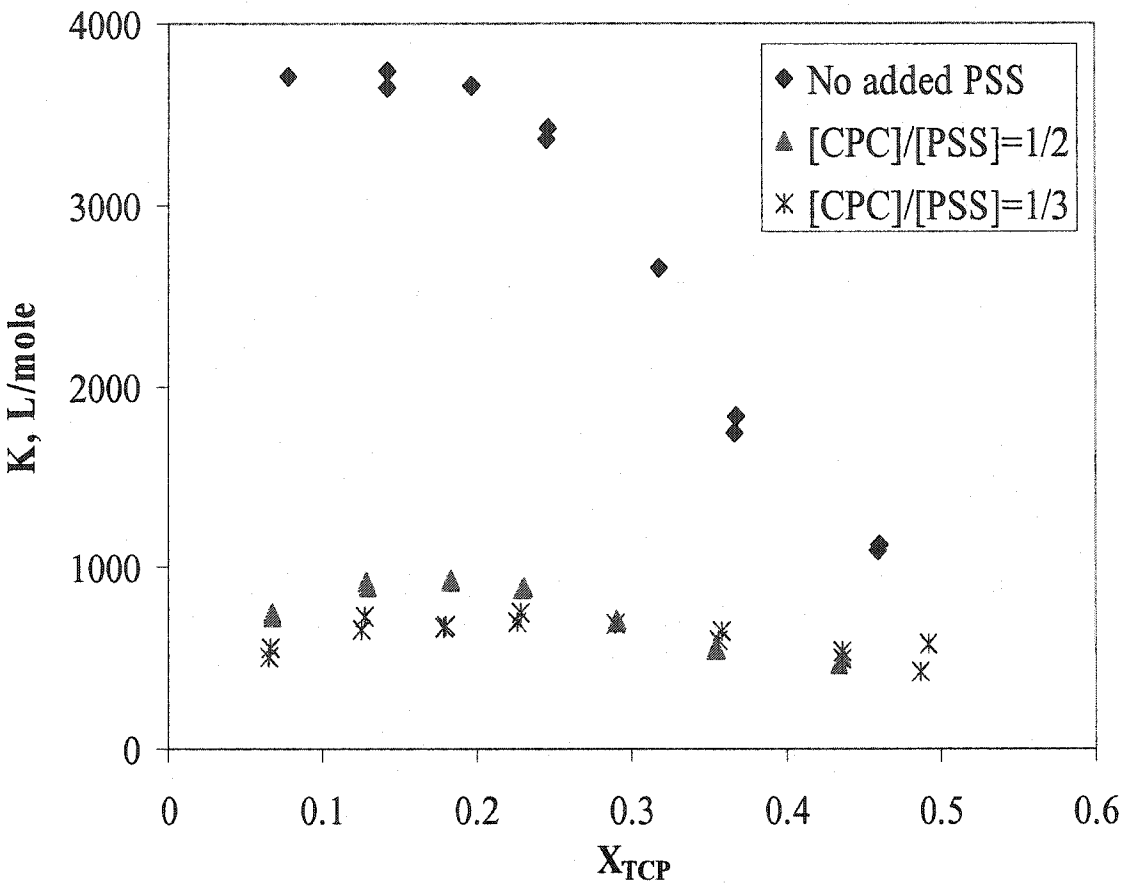


Figure 3. 13 Solubilization equilibrium constant of TCP vs. mole fraction of TCP in micelle, with and without PSS. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

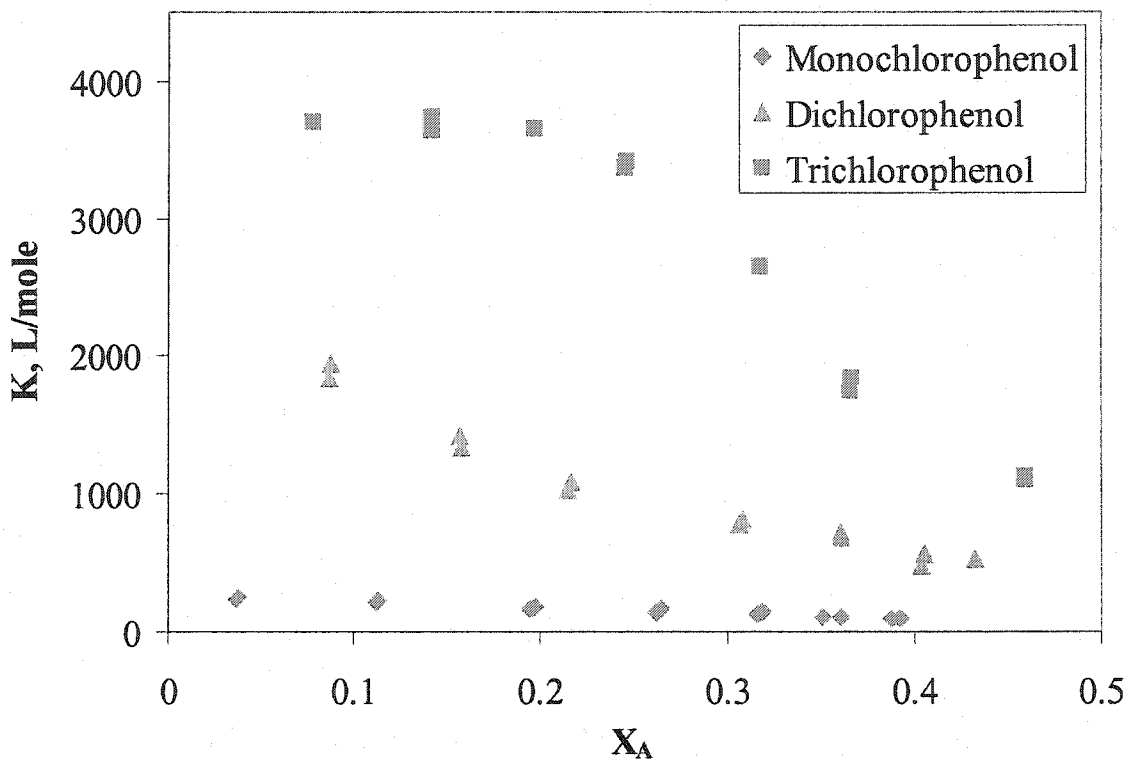


Figure 3. 14 Solubilization equilibrium constant vs. mole fraction of solute in the surfactant micelle. Initial [CPC] is 25 mM (no added PSS).

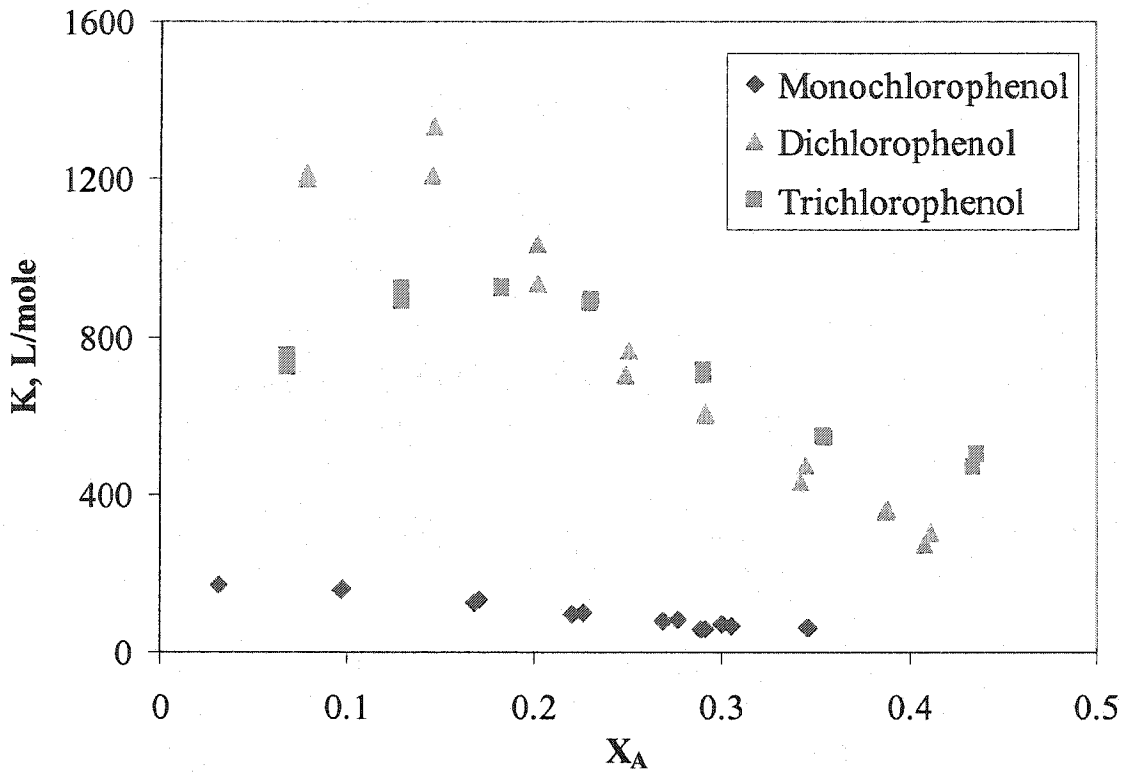


Figure 3. 15 Solubilization equilibrium constant vs. mole fraction of solute in the surfactant - polymer complex. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

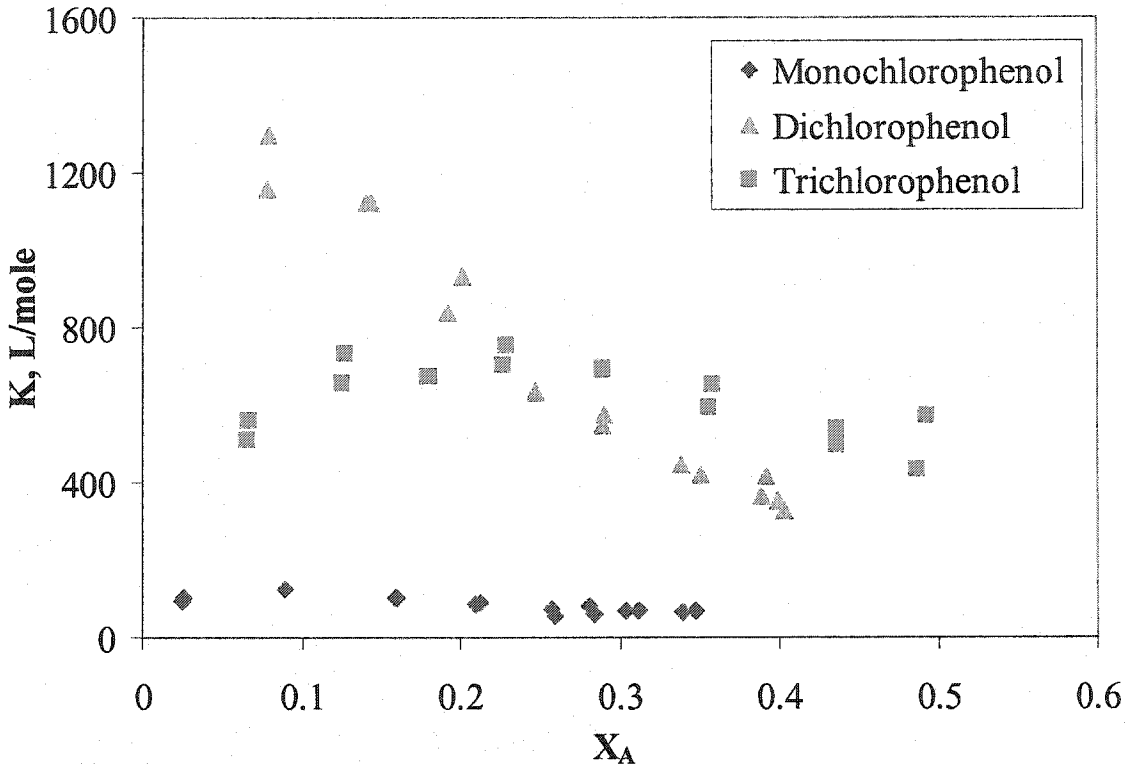
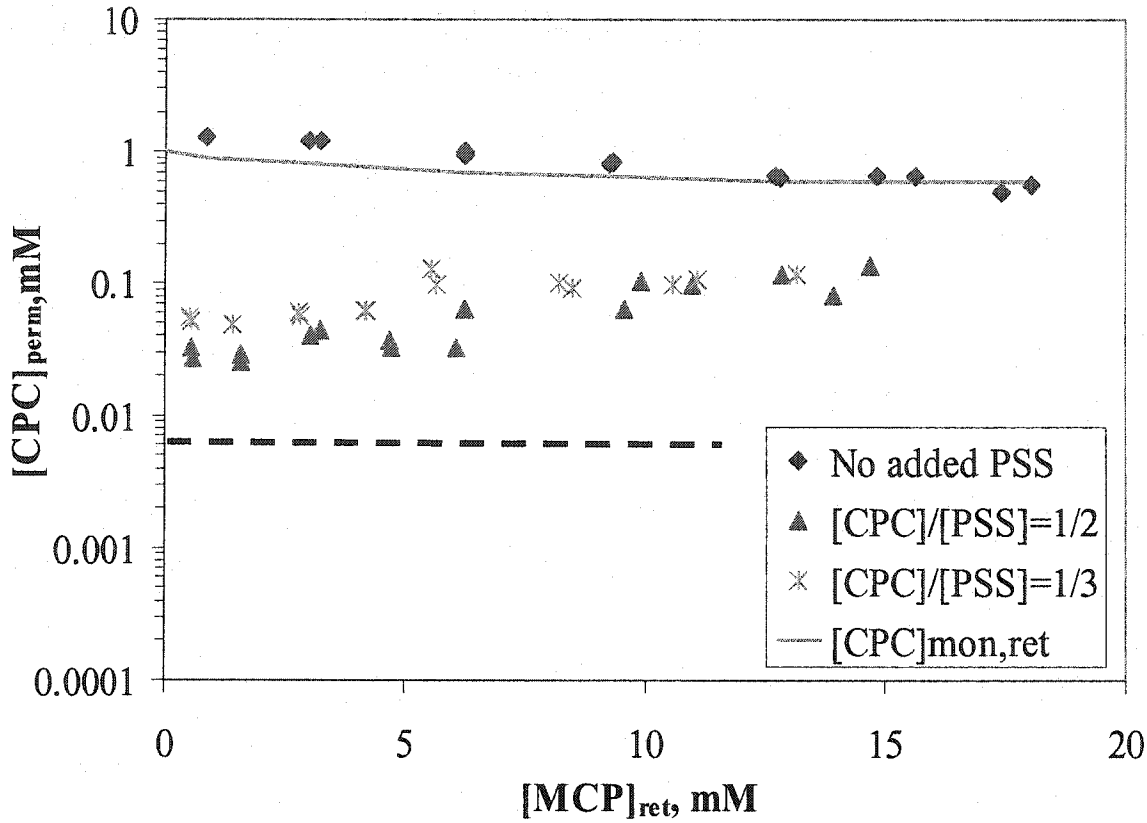
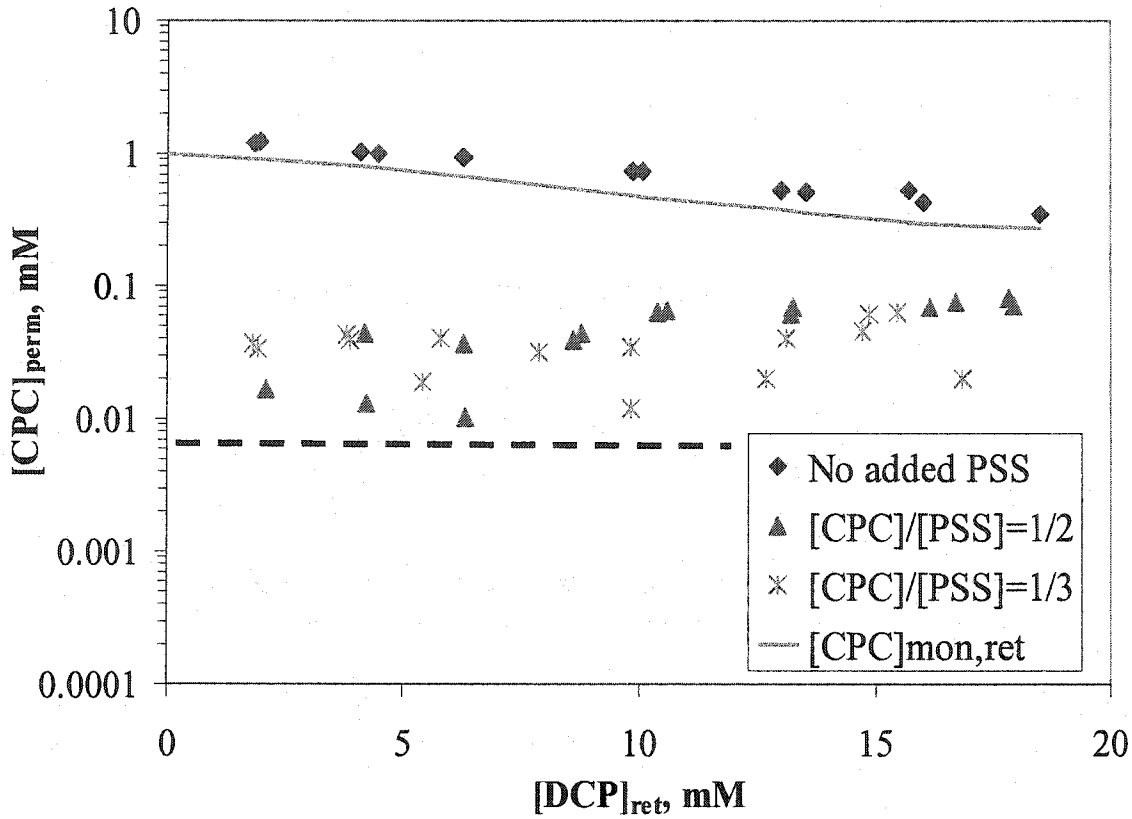


Figure 3. 16 Solubilization equilibrium constant vs. mole fraction of solute in the surfactant - polymer complex. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively.



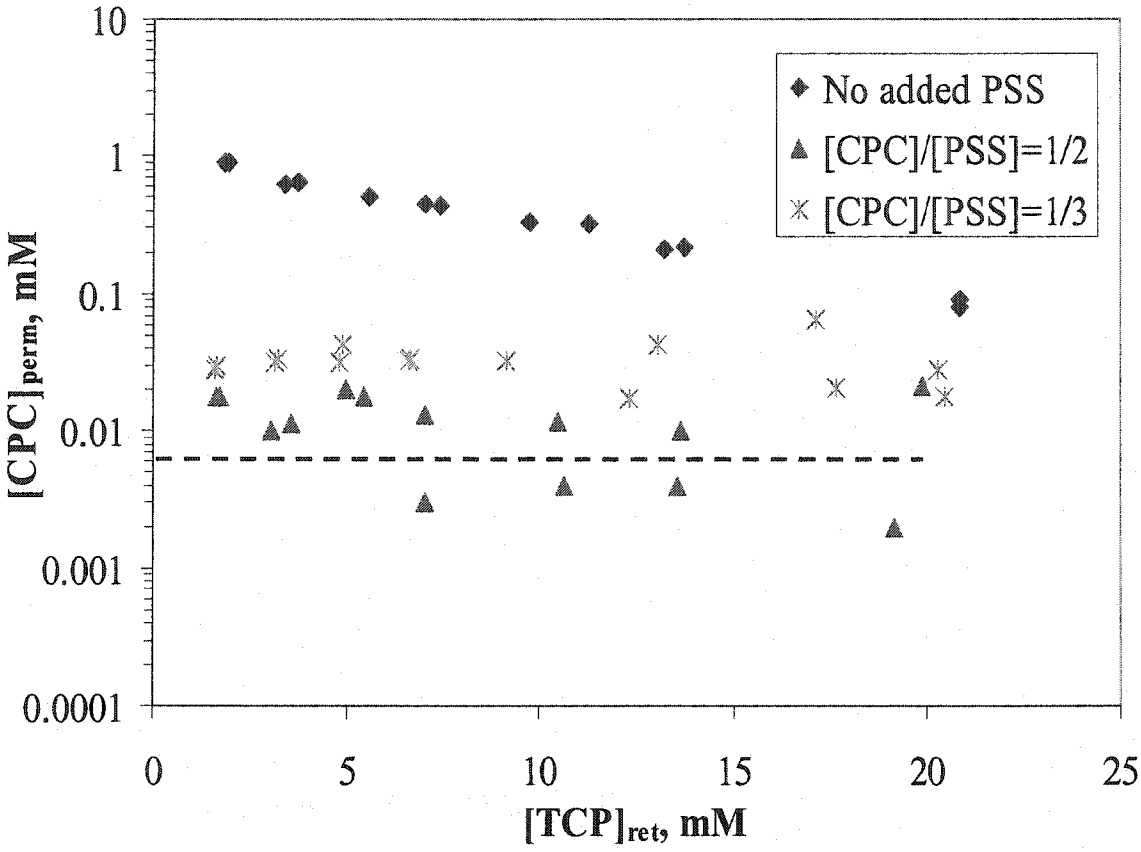
- - - $[CPC]_{monomer}$ in the CPC - PSS mixture (50 mM PSS) at zero solute concentration

Figure 3. 17 CPC concentration in the permeate vs. MCP concentration in the retentate. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).



- - - $[CPC]_{monomer}$ in the CPC - PSS mixture (50 mM PSS) at zero solute concentration

Figure 3. 18 CPC concentration in the permeate vs. DCP concentration in the retentate. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).



– – – $[CPC]_{monomer}$ in the CPC - PSS mixture (50 mM PSS) at zero solute concentration

Figure 3. 19 CPC concentration in the permeate vs. TCP concentration in the retentate. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3).

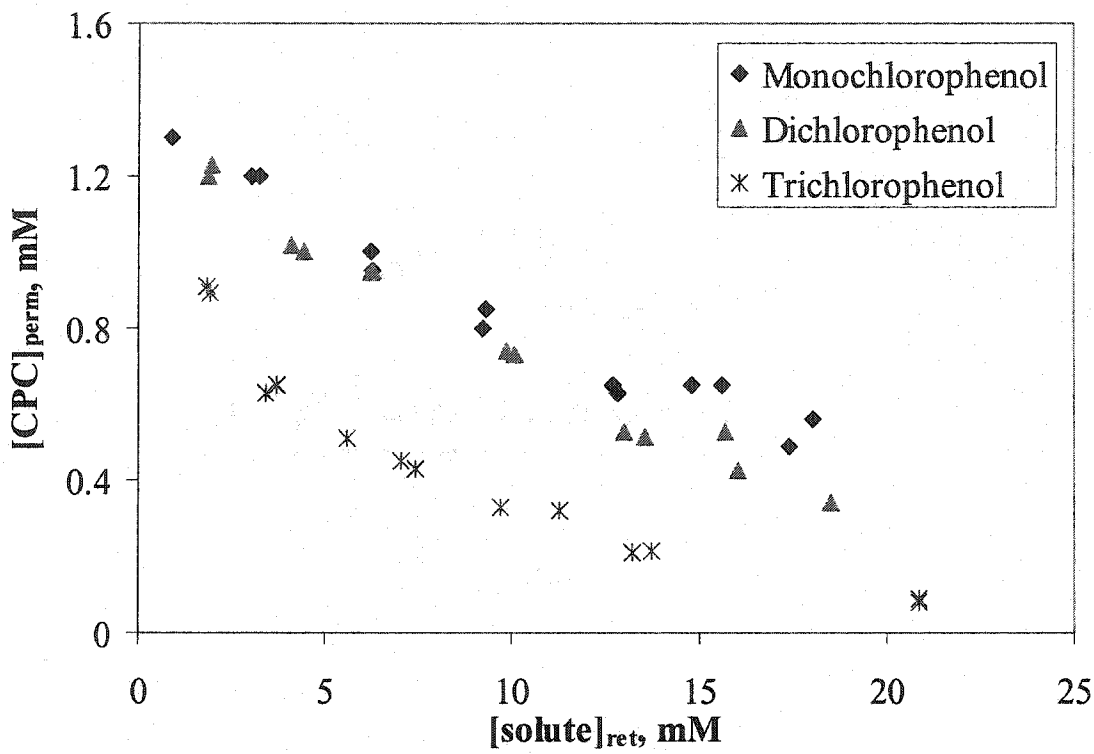


Figure 3. 20 CPC concentration in the permeate vs. solute concentration in the retentate. Initial [CPC] is 25 mM (no added PSS).

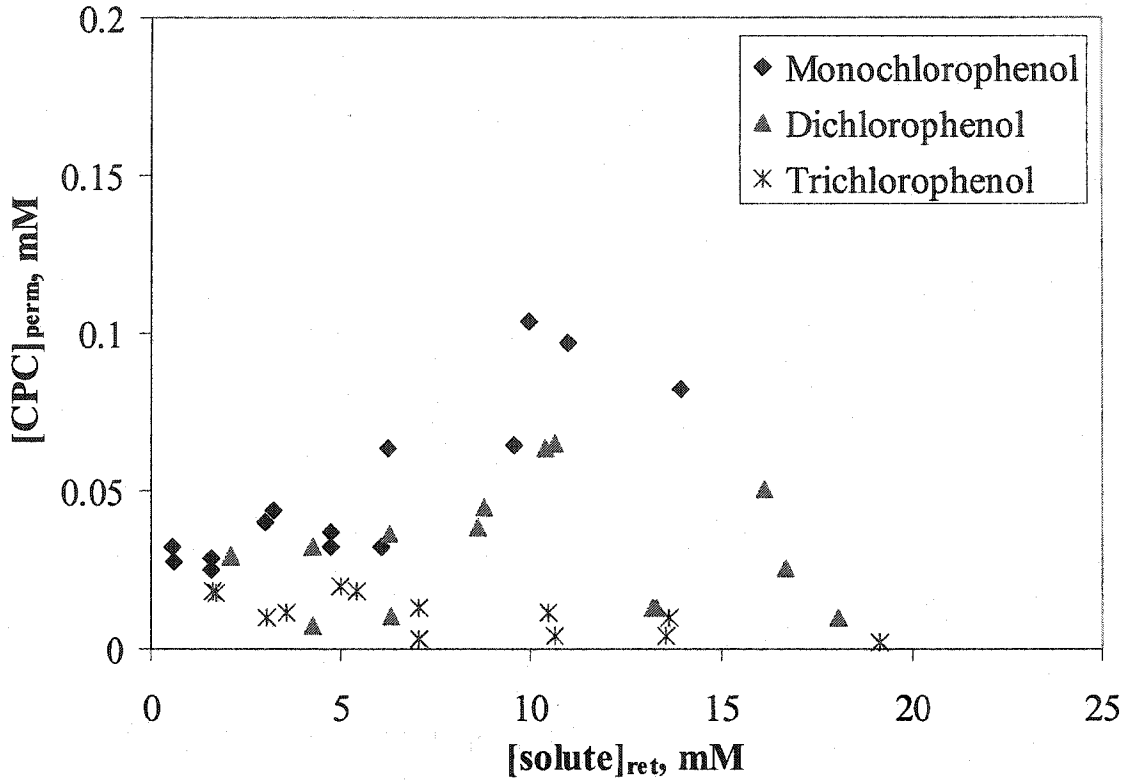


Figure 3. 21 CPC concentration in the permeate vs. solute concentration in the retentate. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

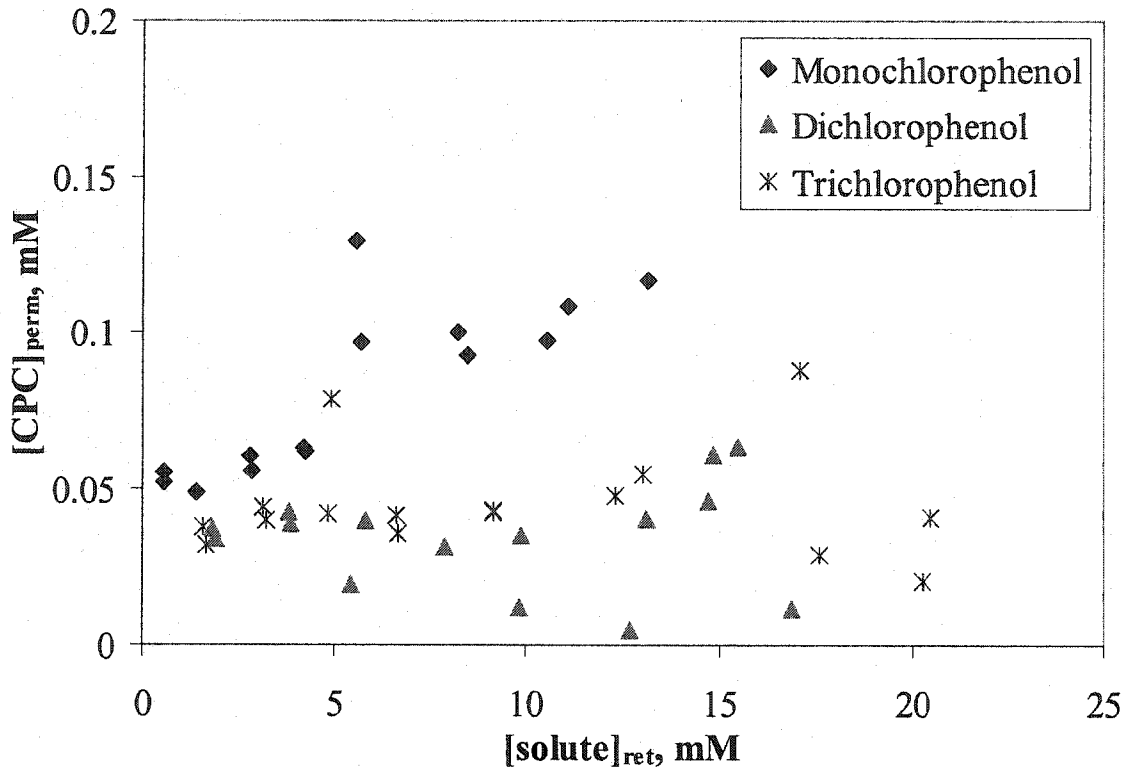


Figure 3. 22 CPC concentration in the permeate vs. solute concentration in the retentate. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively.

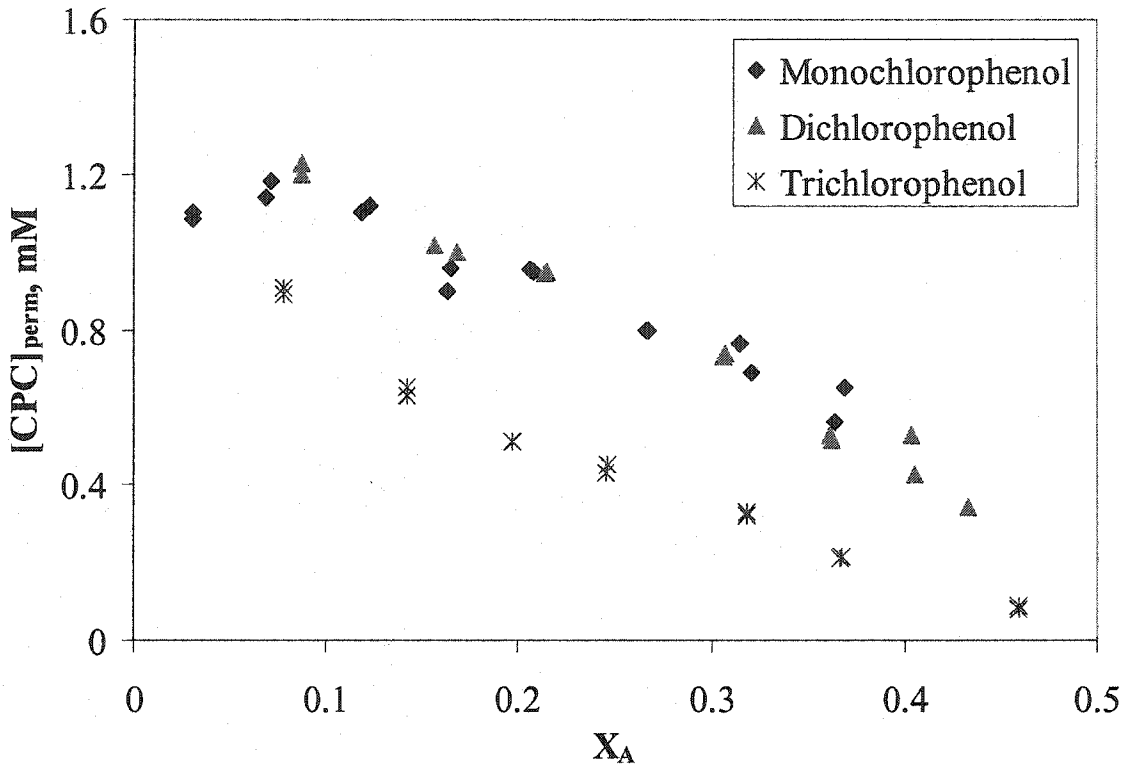


Figure 3. 23 CPC concentration in the permeate vs. mole fraction of the solute in the micelle. Initial [CPC] is 25 mM (no added PSS).

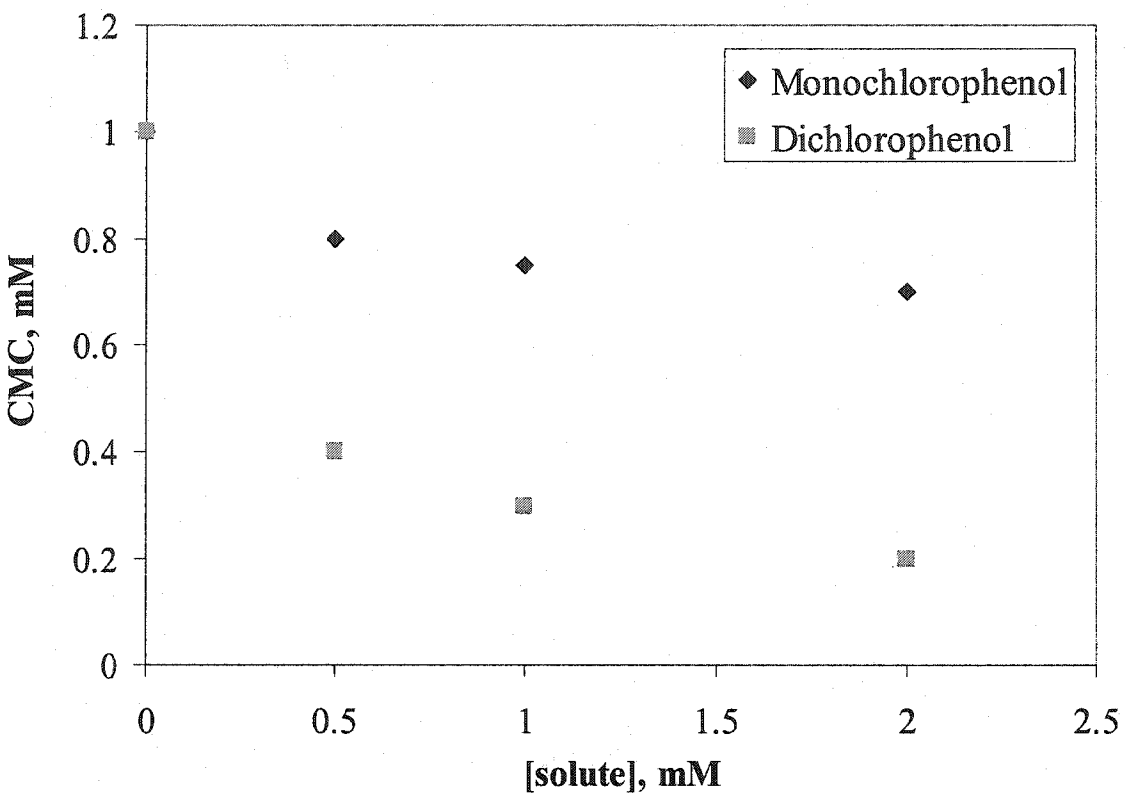


Figure 3. 24 CMC value of CPC vs. solute concentration.

CHAPTER 4

APPARENT ACID DISSOCIATION CONSTANS OF CHLOROPHENOLS IN COLLOID SOLUTIONS AT DIFFERENT IONIC STRENGTH AND EFFECT OF PH ON SOLUBILIZATION OF PHENOLIC COMPOUNDS

4.1 Abstract

The apparent acid dissociation constants ($K_{a,\,app}$) of three phenolic solutes are determined in surfactant solutions and surfactant - polymer mixtures at different salinities by using a spectrophotometric titration technique: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). The distribution coefficients of charged species and neutral species of MCP into micelles and into surfactant - polymer complexes are also investigated. Cetylpyridinium chloride (CPC) is the cationic surfactant and sodium polystyrenesulfonate (PSS) is the anionic polymer used. Semiequilibrium dialysis (SED) is used to determine the distribution coefficients of MCP as well as the solubilization constant of TCP in the colloid solution. The effect of pH or species charge on the solubilization constant of TCP is focused on here. It is observed that the apparent pK_a value of the solutes in the micellar solution is less than the value in the aqueous solution, whereas the apparent pK_a value of the solutes in the surfactant - polymer mixtures is higher than that in the aqueous solution and the micellar solution. The apparent pK_a value increases as salt

concentration increases in the micellar solution while remaining almost unchanged in the surfactant - polymer mixtures. In the micellar solution, the distribution coefficient into the surfactant aggregate of the anionic species is higher than that of the neutral species because the electrostatic interaction between the surfactant head groups and the phenolate anion enhances the solubilization; however the distribution coefficient of the neutral species is higher than that of the charged species in the surfactant - polymer mixtures. In the micellar solution, the distribution coefficient of the neutral species is less dependent on salinity than that of the charged species. The distribution coefficient of the charged species in the micellar solution decreases by almost 50% when salt concentration increases from 0.05 M to 0.1 M.

4.2 Introduction

Several studies from our group have been done to investigate the ability of surfactant micelles[46-51] and surfactant - polymer complexes[43-45] to solubilize polar organic compounds. It was found that ordinary cationic micelles can solubilize a polar ionizable organic solute to a greater extent per aggregated surfactant molecule than the cationic surfactant/anionic polymer complexes[42,45]. This was attributed to the reduction in electrostatic potential at the surface of surfactant aggregates through neutralization by the oppositely charged polymer.

Not only does the solubilization equilibrium constant depend on the type of colloid, but it also relies on the solute characteristics such as hydrophobicity or water

solubility and polarity. For chlorophenols, increasing the number of chlorine atoms per molecule results in higher acidity, but lowers the dipole moment[42]. In micellar solution, solutes with a higher acidity (lower pK_a) or lower water solubility can be solubilized in a greater amount than solutes with a low acidity or high water solubility. This type of behavior has been demonstrated in studies using micellar-enhanced ultrafiltration or MEUF[42,45,46,112,116]. However, in surfactant - polymer systems, ion-dipole interactions may also play an important role in solubilization. For instance, although the water solubility of trichlorophenol (TCP) is less than dichlorophenol (DCP)[42], the solubilization constant of DCP is higher than that of TCP at low solute concentration due to a higher dipole moment of DCP than TCP.

In general, the solubilization constant of polar organic solutes decreases as the extent of solute loading increases[42-49,51]. This characteristic suggests that the solute is initially located at the micellar surface at low solute concentration. Once all the active sites are occupied, solubilization may occur in the palisade region. For ionizable solutes such as phenols, electrostatic interactions may occur between the negative charge on the oxygen atom and the cationic surfactant head groups, which should increase the partition of phenolate anion towards the micellar phase. In contrast, repulsive interactions would occur between phenolate anion and sodium dodecylsulfate (SDS). Therefore, if the ionized organic solute has a charge opposite to that of the surfactant head groups, the solubilization ability is further enhanced. Thus, the solubilization depends on the pH of the solution and the pK_a of organic solutes like chlorophenols.

The acid dissociation reaction of chlorophenolic compounds (HCP) and the associated equilibrium constant expressions are shown in the following equations

$$\mathrm{HCP} \overset{K_a^C}{\rightleftharpoons} \mathrm{H^+ + CP^-} \tag{4.1}$$

$$K_a^T = \frac{a_H a_{CP^-}}{a_{HCP}} = \frac{[H^+][[CP^-]}{[HCP]} \frac{\gamma_{H^+}\gamma_{CP^-}}{\gamma_{HCP}} \tag{4.2}$$

$$K_a^T = K_a^C \frac{\gamma_{H^+}\gamma_{CP^-}}{\gamma_{HCP}} \tag{4.3}$$

where K_a^T is the thermodynamic equilibrium constant, K_a^C is the concentration equilibrium constant expressed in units of mol/L, and γ_i is the activity coefficient of species "i" in solution.

The thermodynamic equilibrium constant does not depend on the concentration of the reacting substances. However, the value of the concentration equilibrium constant varies with concentration to an extent that depends on the deviation of the reacting substances from ideality shown by Eq. (4.2). The activity coefficient of an ion depends on the ionic strength (I) and can be calculated by using the Davies equation[141]. However, for an uncharged species, the salt effect is usually relatively small. In the absence of salt, the behavior of a non-electrolyte is almost ideal in

aqueous solution. The activity coefficients differ from unity by approximately ± 0.05[141], although deviations from ideality become appreciable at salt concentrations greater than 1 M. In the presence of salt, the activity coefficient (γ_N) of a non-electrolyte N may be expressed as a function of the electrolyte and non-electrolyte concentrations, C_S and C_N, respectively, at a given temperature.

$$\log \gamma_N = K_S C_S + K_i C_N \tag{4.4}$$

where K_S is the salting-out or ion-nonelectrolyte interaction parameter and K_i is the self interaction parameter[142]. In cases where C_N is much smaller than C_S, the self interaction term can be neglected. The K_S value determined for *p*-chlorophenol in aqueous NaCl is approximately 0.175 at 25° C[143], which is in agreement with the value obtained using Setchenow's model[144].

Using the K_S value of 0.175 at [NaCl] = 0.1 M, the calculated activity coefficient (γ_{HCP}) obtained using Eq. (4.4) is 1.041. By assuming that $\gamma_{HCP} \approx 1$ and rearranging Eq. (4.3), one obtains the following relationship

$$K_a^C = \frac{K_a^T}{\gamma_{H^+}\gamma_{CP^-}} = \frac{1}{K_H} \tag{4.5}$$

K_a^C can be determined by from spectrophotometic titration data[145-147]. Absorbance can be obtained at different pHs, then K_H can be obtained using following expression

$$Abs_i = \frac{Abs_L + Abs_{HL} K_H (10^{-pH})}{1 + K_H (10^{-pH})} \tag{4.6}$$

where Abs_i is the measured absorbance at a given wavelength, Abs_L and Abs_{HL} are the limiting absorbances of the basic and acidic forms of the solute, respectively, K_H is the protonation constant ($pK_a = \log K_H$), and pH is the observed pH of the solution.

The distribution of hydrophobic ionizable organic compounds between the aqueous and nonaqueous phases depends on the pH and ionic strength of the aqueous phase [148-151]. Previous studies with chlorophenols[42,45,46] have shown that increasing the number of chloro substituents leads to an increase in partitioning of the solutes into the colloidal phase and an increase in the hydrophobicity. Hence, phenols with more chloro constituents are more likely to be ionized at a given pH value and are intrinsically more hydrophobic. However, for nitrophenols, although the nitro substituent causes an increase in acidity of the phenols, the substituent causes much less hydrophobicity than the chloro substituent[148].

The acid dissociation reactions for solutes in micelles have been investigated by several groups[146,147,152-156] who found shifts of the apparent pK_a values for both charged and uncharged micelles. The apparent pK_a shift is attributed partly to the low dielectric constant at the micellar surface and partly to the electrical potential at the surface of the charged micelles[152]. In addition, Underwood suggested that pK_a shifts are interpretable in terms of the influence of micelle charge on the work required for proton removal from the micellar surface to the bulk solution[153]. The apparent pK_a of a weak acid or weak base residing in the vicinity of a charged interface is generally composed of an electrostatic component due to the surface potential and an inherent interfacial non-electrostatic component. This relationship is often expressed[155,156] as

$$pK_a = pK_a^0 - \frac{F\psi}{2.303RT} \tag{4.7}$$

$$pK_a = pK_a^0 - \frac{\psi}{59.16} \tag{4.8}$$

where pK_a^0 is the apparent pK_a of the molecule in the absence of any potential (i.e., the intrinsic pK_a), ψ is the mean field potential (in mV) at the average interface site of residence for the prototropic moiety, F and R are the Faraday and gas constants, respectively, and T is the absolute temperature. Mukerjee and Banerjee interpreted pK_a values in terms of the overall $[H^+]$ in bulk solution[147]. The $[H^+]$ at the surface is different due to the electrical potential difference of the surface with respect to bulk solution.

The main objectives of this study are to investigate the effect of surfactant micelles, surfactant - polymer complexes, and ionic strength on the apparent pK_a of chlorophenolic solutes with different degrees of chlorination, and to calculate the distribution coefficients of such solutes for both neutral and charged species. These results then help interpret the effect of pH level at a given ionic strength on the solubilization constant of a phenolic solute (TCP) obtained from SED experiments carried out.

4.3 Experimental

4.3.1 Materials

Detailed description of the materials was described previously in section 3.3.1. Sodium chloride (certified A.C.S.) from Fisher Scientific (Fair Lawn, NJ) is used as an added salt.

4.3.2 Methods

Spectrophotometric titrations were carried out to determine the protonation constant (K_H) for the organic solutes in micellar solutions and surfactant-polymer mixtures in both the presence and absence of added NaCl at room temperature (controlled at 25 °C). Spectra were obtained using the spectrometer described previously[42] with a 1.0 cm pathlength cuvet. Deionized water at several pHs was used to prepare solutions for the analysis. The pH of the solutions was recorded before performing the UV analysis. Using measured absorbance values at different pHs, the value of K_H was determined by non-linear least-squares analysis using Eq. (4.6)[157,158]. The species distribution of the solutes was obtained using the pK_a (= log K_H) values as described previously[42].

The semiequilibrium dialysis (SED) method was used to measure solubilization as seen in Chapter 3. Detailed description of the SED experiment was

described in section 3.3.2. Only difference is that, for the system with salt, solution containing NaCl at a concentration identical to that in the retentate was placed in the permeate compartment.

To study the effect of pH on the solubilization value of a solute (TCP), two initial pH levels were chosen in order to obtain different charge distributions. To avoid membrane degradation, a pH value of 3.0 was chosen as the lower limit for these studies. At this pH, the solutions predominantly contain the neutral species. The initial pH of the permeate and retentate solutions was set at 3.0. Preparation of colloid solutions at higher pH is difficult because the colloid solutions turn yellow as NaOH is added, presumably due to CPC degradation. Therefore, the solutions at higher pH were obtained without pH adjustment. The pH values of initial and final retentate solutions were measured.

4.4 Results and Discussion

4.4.1 Apparent pK_a Values

Plots of absorbance versus pH for MCP, DCP, and TCP are shown in Figs. 4.1 through 4.3, for the wavelengths at which the maximum absorbance changes occur during the spectrophotometric titrations. In the micellar solutions, the titration curves shift to a higher pH as the NaCl concentration increases. However, the added salt has a negligible effect on the titration curves of the solutes in the surfactant - polymer

mixtures. The observed pK_a values of the solutes in the micellar solutions and the surfactant - polymer mixtures are listed in Table 4.1. In water, the observed pK_a values increase in the order TCP < DCP < MCP. In the CPC solutions with no added salt, the observed pK_a values follow the same order. Likewise, in the presence of 0.05 M and 0.1 M NaCl, the pK_a values of the solutes maintain the same order found in the water and micellar systems. In contrast to the behavior found in the CPC systems, the apparent order of the pK_a values for MCP and DCP in the CPC - PSS systems is reversed, and the pK_a of the solutes in the CPC - PSS mixtures increase in the order TCP < MCP < DCP, both in the absence and presence of the added salt

In the CPC solutions with no added salt, the observed pK_a of a given solute is lower than the corresponding value in water. In the presence of 0.05 M and 0.1 M salt, the observed pK_a values in the CPC solutions increase but remain lower than the value in the aqueous system without CPC. The presence of 0.1 M NaCl increases the pK_a value of the solutes by almost 1 unit in the micellar solutions. However, at the same concentration, the added salt does not affect the pK_a of the solutes in the CPC - PSS mixtures. It should be noted that the pK_a values of the solutes in the CPC - PSS mixtures are higher than those in the water system and the micellar solutions. For a given solute, the pK_a values follow the order $pK_{a,micelle} < pK_{a,water} < pK_{a,surfactant\text{ - }polymer}$.

In the CPC - PSS systems, both in the absence and the presence of the added salt, the pK_a value of MCP and DCP is relatively high (> 9). At this pH or higher, the solution turns yellowish due to CPC degradation; therefore the determination of the pK_a value is unreliable. This unreliability makes it difficult to distinguish the order of

MCP and DCP because their pK_a values are close to each other (the difference between the pK_a values of MCP and DCP in water is 0.56 whereas the difference between MCP and TCP is 2.26).

In micellar solutions without salt, the cationic surfactant head groups should interact preferentially with the phenolate anion. Therefore, at a given bulk pH, the solute is more likely to be ionized, thus reducing the apparent pK_a. In contrast, ion expulsion between the negatively charged surfactant - polymer aggregates and the phenolate anion occurs in the surfactant - polymer mixtures. As a result, the solute becomes less ionized, thus increasing the apparent pK_a. For example, the pK_a values of TCP in micellar solution, water, and surfactant - polymer mixtures are 3.91, 6.14, and 7.52, respectively.

Underwood has also observed large pK_a shifts for a number of acids and bases in ionic micelles[153-154]. He found that pK_a is increased by anionic micelles but it is decreased by cationic micelles. Soto and Fernandez found a similar trend where the pK_a values of a given organic solute in hexadecyltrimethyammonium bromide or CTAB (cationic surfactant), octylphenol ethylene oxide or Triton X-100 (nonionic surfactant), and sodium dodecyl sulfate or SDS (anionic surfactant) are 6.88, 7.58, and 9.92, respectively[156]. Such shifts can be attributed to the effect of surface polarity and electrical potential on the dissociation of the solutes bound to micelles and surfactant - polymer aggregates. It was found that the surface potentials of CTAB and SDS are +155 mV and -125 mM, respectively[156]; and according to Eqs. (4.7) and (4.8), the pK_a value for a given solute in a cationic micelle is smaller than that in an anionic micelle.

This corresponds with the observed values of chlorophenols in CPC - PSS mixtures, where the pK_a values in aggregates having a net negative charge are larger than the corresponding values in cationic micelles. The addition of electrolyte has been found to influence the partition coefficients, acid dissociation constants, and activity coefficients[143,146,150]. The latter can be estimated using the Davies equation[141].

$$-\log\gamma = 0.5Z_i^2\left(\frac{I^{1/2}}{1+I^{1/2}} - 0.3I\right) \tag{4.9}$$

where Z_i is the charge of the ions taking part in the reaction. For a monovalent ion at an ionic strength of 0.1 M, the activity coefficient is 0.785, resulting in a decrease in pK_a^C of 0.21 compared to pK_a^T. However, as mentioned previously, the pK_a value observed in the micellar solution increases by one log unit in the presence of 0.1 M salt. This contradiction can be associated with the presence of the ionic micelle. The presence of both salt and an ionic micelle may affect the apparent pK_a value for the system shown by the following equilibria,

$$HCP_{(aq)} \overset{K_{a,aq}}{\rightleftharpoons} H^+_{(aq)} + CP^-_{(aq)} \tag{4.10}$$

$$HCP_{(aq)} \overset{K_{D,HCP}}{\rightleftharpoons} HCP_{(coll)} \tag{4.11}$$

$$CP^-_{(aq)} \overset{K_{D,CP^-}}{\rightleftharpoons} CP^-_{(coll)} \tag{4.12}$$

where $K_{a,aq}$ is concentration equilibrium constant at a given ionic strength in aqueous and nonaqueous phases (colloidal phase), respectively, and $K_{D,HCP}$ and K_{D,CP^-} are distribution coefficients (vol/vol) between colloid and aqueous phases for the protonated (HCP) and unprotonated forms (CP^-) of the solute, respectively. From the equilibria above, we obtain,

$$K_{a,aq} = \frac{[H^+]_{aq}[CP^-]_{aq}}{[HCP]_{aq}} \tag{4.13}$$

$$K_{D,HCP} = \frac{[HCP]_{coll}\left(V_{aq}/V_{coll}\right)}{[HCP]_{aq}} \tag{4.14}$$

$$K_{D,CP^-} = \frac{[CP^-]_{coll}\left(V_{aq}/V_{coll}\right)}{[CP^-]_{aq}} \tag{4.15}$$

where V_{aq} is the volume in the aqueous phase and V_{coll} is the volume of the colloid phase (or organic phase). The apparent acid dissociation constant, $K_{a,app}$, can be written as follows[159]

$$K_{a,app} = \frac{[H^+]([CP^-]_{aq} + [CP^-]_{coll})}{([HCP]_{aq} + [HCP]_{coll})} \tag{4.16}$$

combining Eqs. (4.14) and (4.15) with Eq. (4.16) gives

$$K_{a,app} = \frac{[H^+]([CP^-]_{aq} + K_{D,CP^-}[CP^-]_{aq}(V_{aq}/V_{coll}))}{([HCP]_{aq} + K_{D,HCP}[HCP]_{aq}(V_{aq}/V_{coll}))} \tag{4.17}$$

$$K_{a,app} = \frac{[H^+][CP^-]_{aq}}{[HCP]_{aq}}\left(\frac{1 + K_{D,CP^-}(V_{aq}/V_{coll})}{1 + K_{D,HCP}(V_{aq}/V_{coll})}\right) \tag{4.18}$$

$$\frac{K_{a,app}}{K_{a,aq}} = \frac{1 + K_{D,CP^-}(V_{aq}/V_{coll})}{1 + K_{D,HCP}(V_{aq}/V_{coll})} \tag{4.19}$$

As shown in Eq. (4.19), $K_{a,app}$ is affected by the distribution coefficients of the neutral and charged species and these coefficients are dependent on the ionic strength. For the CPC micelles, K_{D,CP^-} is expected to be larger than $K_{D,HCP}$ due to the electrostatic interaction between the cationic surfactant head groups and the phenolate anion. Increasing ionic strength is expected to have only a slight effect on $K_{D,HCP}$. Therefore, the apparent or observed pK_a in micellar solution is smaller than that in water. It is reasonable to expect a decrease in K_{D,CP^-} as the salt concentration increases because of a reduction in the electrostatic interaction between the surfactant head groups and the negatively charged phenolate ion, thus increasing the pK_a value.

This behavior was also seen with indicator dyes solubilized by CTAB[147] where increasing salt concentration causes a decrease in the ψ value, resulting in an increase in the pK_a value. For the CPC - PSS complexes, the aggregates have a net negative charge; therefore, it is plausible that the K_{D,CP^-} value is lower than the $K_{D,HCP}$ value due to the ion-ion expulsion between the negatively charged surfactant - polymer aggregate and the phenolate anion, resulting in $pK_{a,app}$ being greater than $pK_{a,aq}$ (as previously noted). In addition, the effect of ionic strength is diminished by the counterions present in the CPC - PSS mixtures. As a result, the addition of salt does not significantly influence the apparent pK_a.

4.4.2 Distribution Coefficients

The distribution coefficient of the neutral species ($K_{D,HCP}$) can be obtained from SED experiments, as shown in following equation, using data at low solute concentrations and at a pH low enough to minimize the concentration of the anionic form (CP^-)

$$K_{D,HCP} = \left(\frac{[HCP]_{ret} - [HCP]_{perm}}{[HCP]_{perm}} \right) \left(\frac{V_{aq}}{V_{org}} \right) \tag{4.20}$$

where $[HCP]_{ret}$ and $[HCP]_{perm}$ are solute concentrations in the retentate and the permeate obtained from SED experiment described previously. The value of K_{D,CP^-} could be determined from Eq. (4.19) with the known values of $K_{D,HCP}$, $K_{a,app}$, $K_{a,aq}$, and V_{aq}/V_{coll}. It was found that the partial molar volume for CPC in the presence of 0.03 M salt is 380 cm^3/mole; in addition, the added salt had no significant effect on the molar volume[160]. In the CPC - PSS mixtures, Skerjanc and Kogej found that the molar volume of the CPC - PSS mixtures at 1/2 mole ratio is approximately 224.5 cm^3/mole[161]. Because the product of the distribution coefficient (K_D) and (V_{aq}/V_{coll}) is much greater than unity[145,147,159-163]; Eq. (4.19) may be simplified to give

$$\frac{K_{a,app}}{K_a} \cong \frac{K_{D,CP^-}}{K_{D,HCP}} \tag{4.21}$$

The pH of the initial and final retentate solutions is shown in Table 4.2 and 4.3. The species distribution results in the presence of salt are shown in Figs. 4.4 through 4.6. In the absence of salt, the species distribution results were shown previously

(Figs. 3.6 and 3.7). The percentage of the phenolate anion at the lowest solute concentration is shown in Table 4.4. It is observed that MCP contains predominantly the neutral species except the micellar system without salt which contains 30% phenolate anion. Therefore, as compared to DCP and TCP, MCP is chosen as a model solute to investigate the distribution coefficients. Moreover, the partitioning of DCP and TCP in the colloids is very strong[42], leading to very high distribution coefficient; for example, the K_{D,CP^-} values for DCP and TCP are of the magnitude of 10^5 and 10^6, respectively. As a result, $[HCP]_{perm}$ can be very low, leading to a greater relative error in the calculated value of $K_{D,HCP}$.

From the SED experiments for MCP at the lowest solute concentration, based on the partial molar volumes of CPC micelles and CPC - PSS complexes, we obtain the distribution coefficient of the neutral species ($K_{D,MCP}$) using Eq. (4.20) and the distribution coefficient of the charged species (K_{D,CP^-}), by using Eq. (4.21). The results are listed in Table 4.5.

As seen in Table 4.5, in the micellar solutions, the distribution coefficient for the phenolate anion is higher than that of the neutral species at all salt concentrations. In contrast, the distribution coefficient for the phenolate anion is lower than that of the neutral species in the CPC - PSS mixtures. In the micellar solutions, the phenolate ion tends to partition more strongly than the neutral form due to the electrostatic interaction between the cationic surfactant head groups and the phenolate anion. However, the ion-ion repulsion between the phenolate anion and the negatively

charged surfactant - polymer aggregates contributes to the lower partition coefficient of the phenolate anion than the neutral species.

In the absence of salt, the $K_{D,MCP}$ value is approximately reduced by a factor of two in the CPC - PSS mixture as compared to the value in the CPC solution; however, the reduction of the K_{D,CP^-} caused by the presence of PSS is more pronounced. This is due to fact that the charged species more strongly influence partition coefficients in the surfactant – polymer mixtures than the neutral species.

In the micellar solutions, the distribution coefficient of the neutral species of MCP ($K_{D,MCP}$) is increased by the addition of salt; the $K_{D,MCP}$ value increases from 563 to 1029 when the salt concentration increases from 0 M to 0.05 M. However, the $K_{D,MCP}$ value does not significantly increase as salt concentration increases from 0.05 M to 0.1 M. On the other hand, the distribution coefficient of the charged species (K_{D,CP^-}) decreases by almost a factor of 5 in the presence of 0.05 M salt. The increase in salt concentration from 0.05 M to 0.1 M further decreases the K_{D,CP^-} value, approximately by a factor of two. In the surfactant - polymer mixtures, the added salt does not significantly change the $K_{D,MCP}$ value, but it does decrease the K_{D,CP^-} value by about a factor of 2.

In the micellar solution, the initial addition of salt can increase the micelle size [164-168], therefore increasing the distribution coefficient of the neutral species. The further addition of salt may not significantly enhance the micelle size, and thus the $K_{D,MCP}$ value does not significantly increase. The salting out effect can contribute to

the increase in the distribution coefficient of the neutral species; however, this effect will play an important role only at high salt concentration (greater than 1 M). Westall also found that the distribution coefficient of pentachlorophenol between octanol and water is independent of salt concentration between 0.05 to 0.2 M salt[148]. For the anionic species, the addition of salt has two effects on the partitioning of the anionic solute into the cationic micelles: (1) the electrostatic interaction between the phenolate ion and cationic surfactant head groups is diminished as salt concentration increases; (2) the anion of the added salt competes for "sites" on the micellar surface in an ion exchange type of phenomenon[169]. Similar behavior was also seen in previous studies with ligand-modified polymer untrafiltration (LM-PEUF)[170-171]. For the surfactant - polymer systems, the salt effect on the partitioning of the phenolate anion in the polymer bound micelles is expected to be the same as the micellar systems.

4.4.3 Solubilization Constants

Solubilization constant determination was described previously in section 3.4. Figs. 4.7- through 4.15 show plots of the solubilization constants of TCP as a function of micellar mole fraction of TCP for micellar solutions and surfactant - polymer mixtures at a given salinity. As mentioned previously, the results at high pH range are obtained in the experimental series without pH adjustment whereas the results at low pH range are obtained in the experiment carried out at pH 3. The open symbols are the results obtained from the system without pH adjustment where the pH value varies

with the solute concentration; the lower the solute concentration, the higher the pH. The closed symbols are the results obtained from the systems where both the retentate and permeate solutions are initially at pH 3. The pH shown in the figures (in parenthesis) is the pH of the final retentate solutions. In the micellar solutions, for all salt concentrations, the solubilization constants obtained without pH adjustment or at high pH range (open symbols) are greater than the solubilization constants at pH 3 or at low pH range (closed symbols), as shown in Figs. 4.7 through 4.9. In contrast, for CPC - PSS mixtures, the K values for the high pH range are lower than the corresponding values for series at pH 3, as shown in Figs. 4.10 through 4.15. As the solute concentration increases, the K values of those two series tend to converge for both micellar solutions and surfactant - polymer mixtures.

The difference in the solubilization constants for a given system can be qualitatively interpreted by considering the distribution coefficients and the species distribution. Although the individual distribution coefficients of TCP are not evaluated here, the effect of added salt on the distribution coefficients for TCP as well as DCP follow the same trend as for MCP. In the micellar systems, the solutions at higher pH contain a higher percentage of the charged species than the solution at lower pH. According to the species distribution results, the micellar systems without pH adjustment (open symbols) at the lowest solution concentration contain approximately 56%, 94.4%, and 87.5% of the phenolate anion for the systems shown in Figs. 7, 8, and 9, respectively, as shown in Table 4.4. For the systems at pH 3 (closed symbols), the solutions contain approximately 11%, 2%, and 1% of the

phenolate anion for the system in Figs. 4.7, 4.8, and 4.9, respectively. As shown in Table 4.5, the distribution coefficient of the charged species is higher than that of the neutral species in the micellar solutions, resulting in a greater contribution of the charged species than the neutral species to the solubilization constant. This results in a higher solubilization constant in the system containing the higher percentage of the charged species.

In the surfactant - polymer mixtures, for the systems without pH adjustment (open symbols) at the lowest solution concentration, the mixtures contain 3% and 1% of the phenolate anion for the systems shown in Figs. 4.10 and 4.11, respectively. At pH 3 (closed symbols), zero concentration of charged species is observed. As shown in Table 4.5, the distribution coefficient of the neutral species is higher than that of the charged species in the surfactant - polymer mixture. As a result, the apparent solubilization constants are higher for the systems containing a greater percentage of the neutral species. It should be noted that the percentage of the phenolate anion can change at higher solute concentration. For both micellar and surfactant - polymer systems, as the solute concentration increases, for systems without pH adjustment the pH of the colloidal solution decreases and approaches a pH value of 3. Therefore, the solubilization constants become closer to the values obtained at pH 3 as the solute concentration increases.

Table 4. 1 The observed pK_a values of MCP, DCP, and TCP in water, in 25 mM CPC solutions in the presence of 0, 0.05, and 0.10 M added NaCl, and in the mixture of 25 mM CPC and 50 mM PSS in the presence of 0 and 0.05 M added NaCl (at 25° C).

Water/Colloid solution	[NaCl], M	pK_a		
		MCP	DCP	TCP
Water	0	8.40	7.84	6.14
CPC	0	6.98	6.22	3.91
CPC	0.05	7.76	6.90	4.60
CPC	0.1	7.99	7.08	4.90
CPC - PSS	0	9.09	9.54	7.52
CPC - PSS	0.05	9.15	9.58	7.39

Table 4. 2 The pH value in the initial retentate solutions.

Colloid solutions	[NaCl], M	Initial pH		
		MCP	DCP	TCP
CPC	0	4.6 - 6.0	4.0 - 5.0	2.9 - 3.3
CPC - PSS (1/2)	0	6.3 - 7.0	6.2 - 6.9	5.0 - 5.9
CPC - PSS (1/3)	0	6.5 - 7.0	6.3 - 6.7	4.7 - 6.0
CPC	0.05	4.9 - 6.0	4.8 - 6.4	3.0 - 3.4
CPC - PSS (1/2)	0.05	6.3 - 7.0	6.3 - 6.6	5.1 - 5.6
CPC - PSS (1/3)	0.05	6.3 - 7.0	6.4 - 6.6	4.8 - 5.9
CPC	0.1	5.0 - 6.4	4.6 - 6.5	3.2 - 3.6
CPC - PSS (1/2)	0.1	6.3 – 6.9	6.3 - 6.6	5.0 - 5.6
CPC - PSS (1/3)	0.1	6.3 – 6.9	6.6 - 6.8	4.9 - 5.9

Table 4. 3 The pH value in the final retentate solutions.

Colloid solutions	[NaCl], M	Final pH		
		MCP	DCP	TCP
CPC	0	5.1-6.6	5.1-6.3	3.2-4.0
CPC - PSS (1/2)	0	6.6-6.7	6.2-6.6	5.3-6.0
CPC - PSS (1/3)	0	6.6-6.7	6.2-6.6	5.3-6.0
CPC	0.05	5.5-6.6	5.1-6.3	5.2-5.9
CPC - PSS (1/2)	0.05	6.5-6.6	6.6-6.8	5.4-5.6
CPC - PSS (1/3)	0.05	6.5-6.6	6.6-6.8	5.4-5.6
CPC	0.1	5.8-6.6	5.3-6.4	5.2-5.8
CPC - PSS (1/2)	0.1	6.3-6.9	6.5-6.9	5.7-5.8
CPC - PSS (1/3)	0.1	6.3-6.9	6.5-6.9	5.7-5.8

Table 4. 4 The percentage of the phenolate anion in the final retentate solutions at the highest pH value (the lowest solute concentration) from Table 2 and at pH 3 for TCP.

Colloid solutions	[NaCl], M	Phenolate Anion, %			
		MCP	DCP	TCP	TCP (pH = 3)
CPC	0	30	54	56	11
CPC - PSS (1/2)	0	0	0	3	0
CPC - PSS (1/3)	0	-	-	-	-
CPC	0.05	7	21	94.4	2
CPC - PSS (1/2)	0.05	0	0	1	0
CPC - PSS (1/3)	0.05	-	-	-	-
CPC	0.1	4	17	87.5	1
CPC - PSS (1/2)	0.1	-	-	-	-
CPC - PSS (1/3)	0.1	-	-	-	-

Table 4. 5 The distribution coefficients of MCP in 25 mM CPC solutions in the presence of 0, 0.05, and 0.1 M added NaCl, and in the mixture of 25 mM CPC and 50 mM PSS in the presence of 0 and 0.05 M added NaCl (Subscripts "r" and "p" are retentate and permeate, respectively).

Colloid solutions	[NaCl], M	pH_{feed}	$[MCP]_r$	$[MCP]_p$	$K_{D,MCP}$	$K_{D,CP-}$
CPC	0	6.00	0.916	0.15	563	14821
CPC	0.05	6.05	1.786	0.173	1029	3029
CPC	0.1	6.45	1.715	0.165	1037	1626
CPC - PSS (1/2)	0	6.30	0.928	0.18	241	49
CPC - PSS (1/2)	0.05	6.30	1.628	0.32	237	28

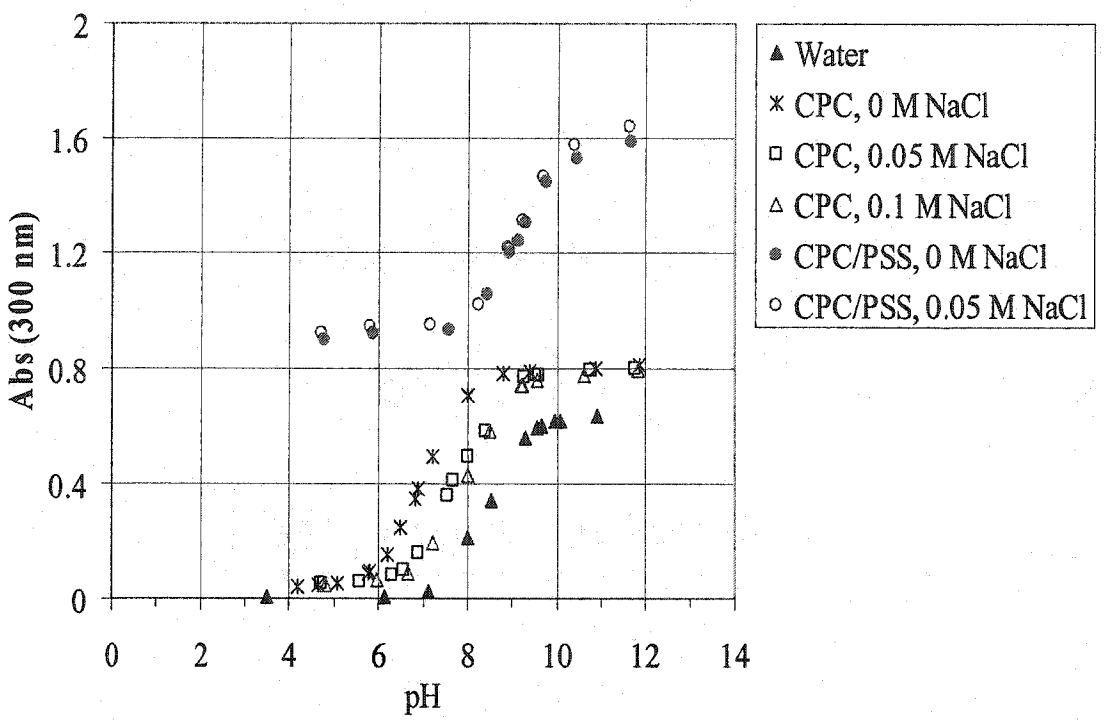


Figure 4. 1 Plots of absorbance vs pH at 300 nm for MCP in water, 25 mM CPC solutions, and the mixture of 25 mM CPC and 50 mM PSS in the absence and presence of 0.05 and 0.1 M NaCl.

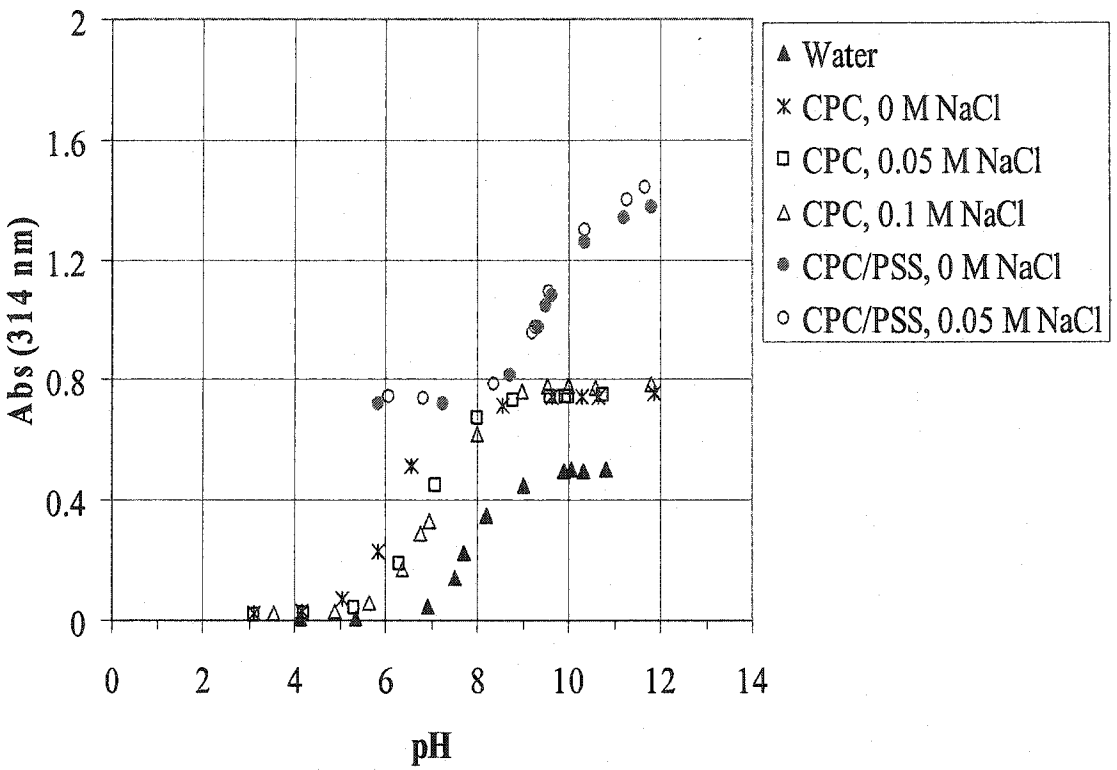


Figure 4. 2 Plots of absorbance vs pH at 314 nm for DCP in water, 25 mM CPC solutions, and the mixture of 25 mM CPC and 50 mM PSS in the absence and presence of 0.05 and 0.1 M NaCl.

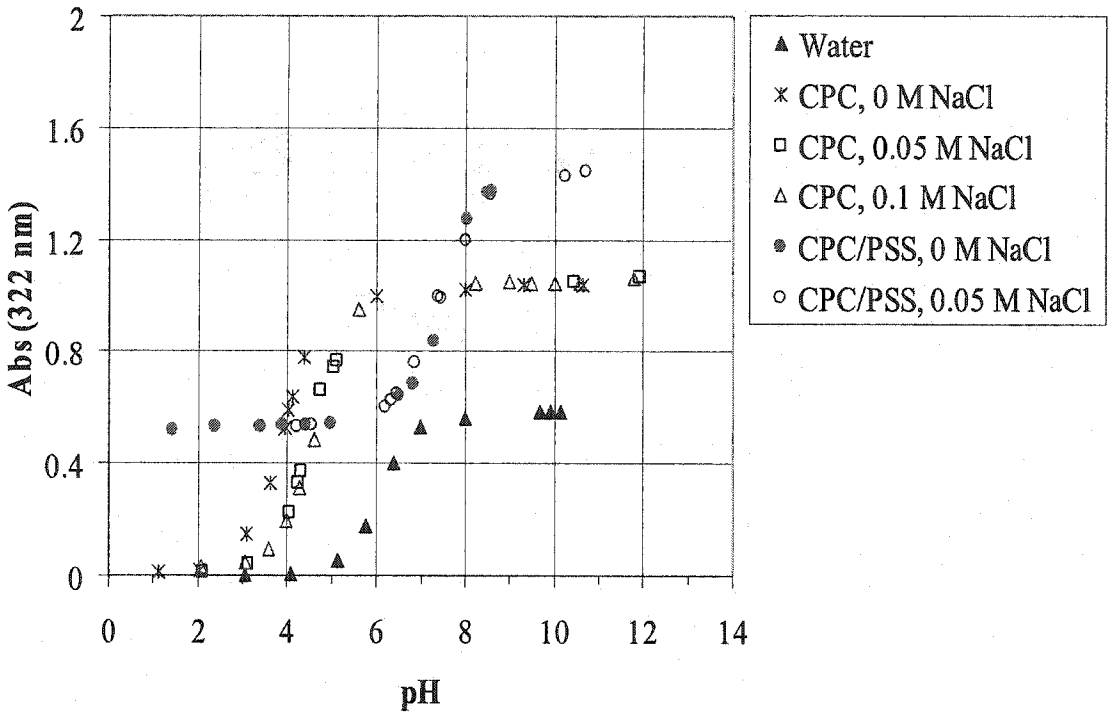
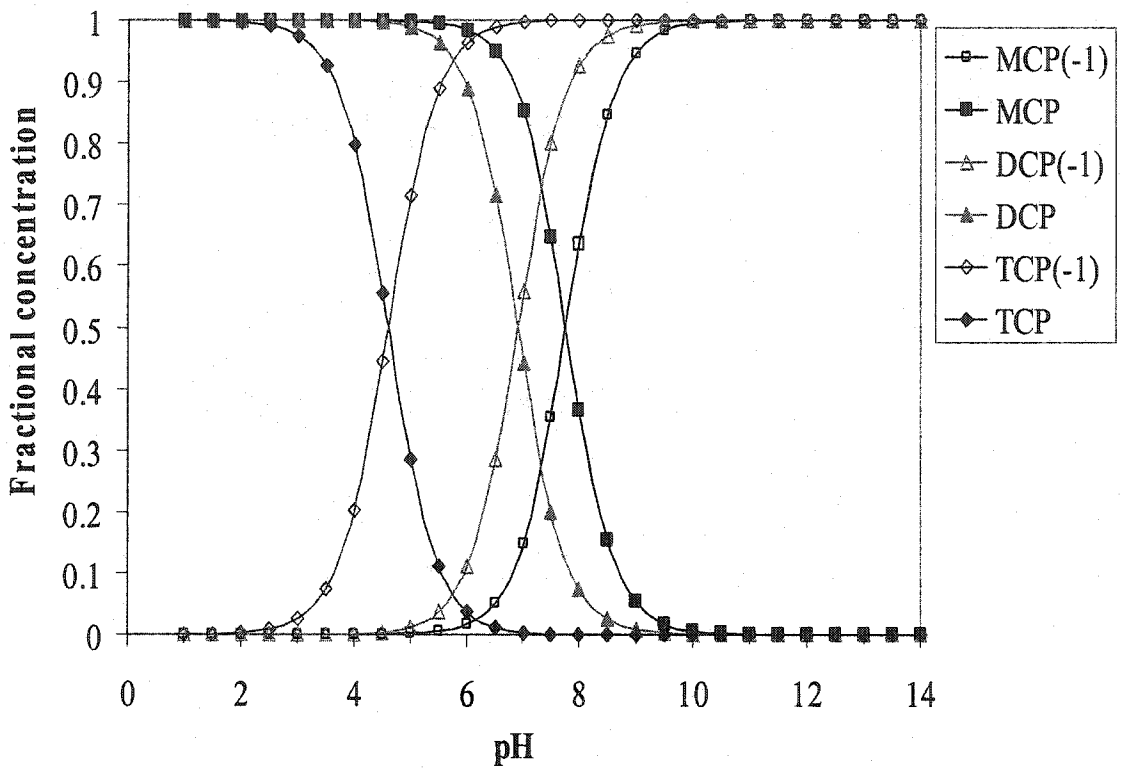
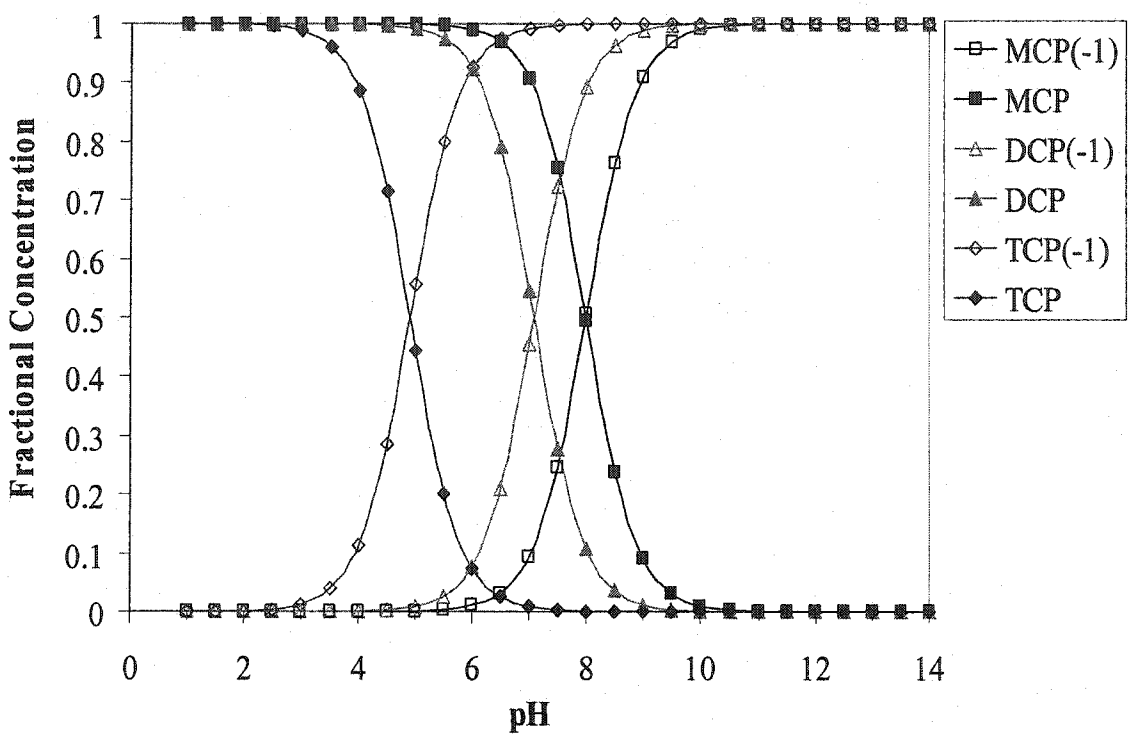


Figure 4. 3 Plots of absorbance vs pH at 322 nm for TCP in water, 25 mM CPC solutions, and the mixture of 25 mM CPC and 50 mM PSS in the absence and presence of 0.05 and 0.1 M NaCl.



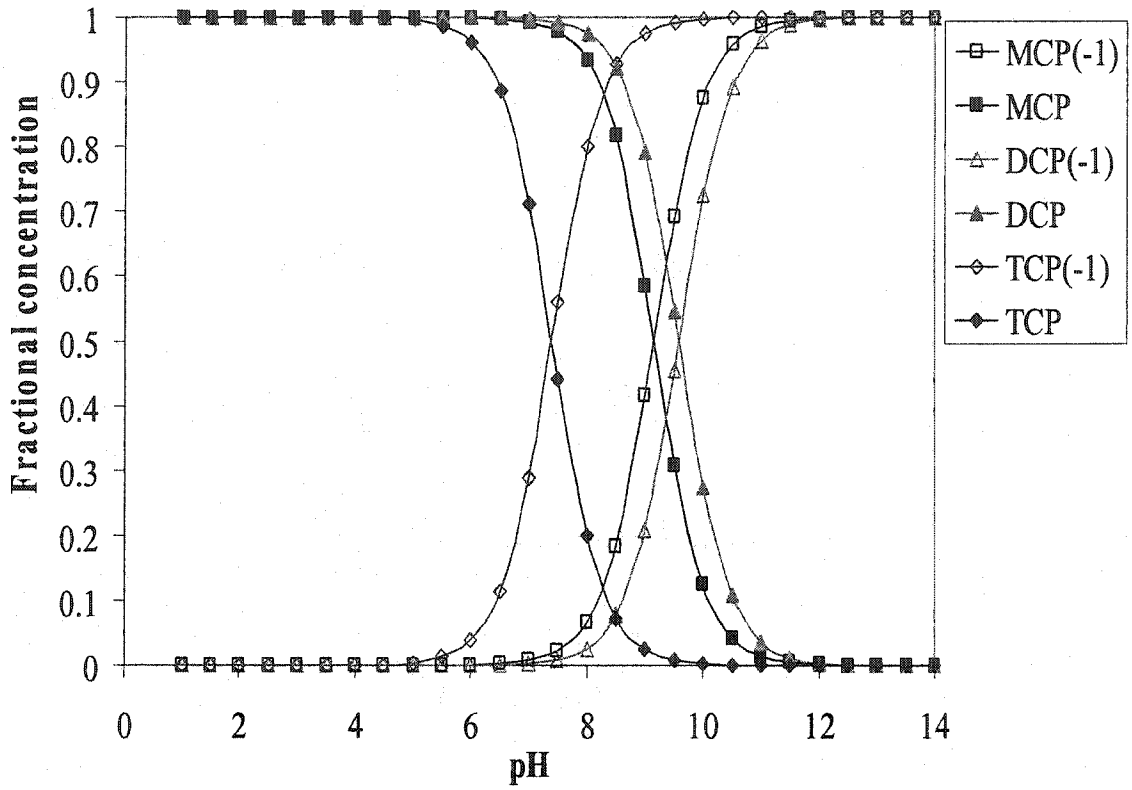
(-1) represents the negatively charged species

Figure 4. 4 Species distribution of MCP, DCP, and TCP in 25 mM CPC solutions in the presence of 0.05 M NaCl.



(-1) represents the negatively charged species

Figure 4. 5 Charge distribution of MCP, DCP, and TCP in 25 mM CPC solutions in the presence of 0.1 M NaCl.



(-1) represents the negatively charged species

Figure 4. 6 Charge distribution of MCP, DCP, and TCP in the mixture of 25 mM CPC and 50 mM PSS in the presence of 0.05 M NaCl.

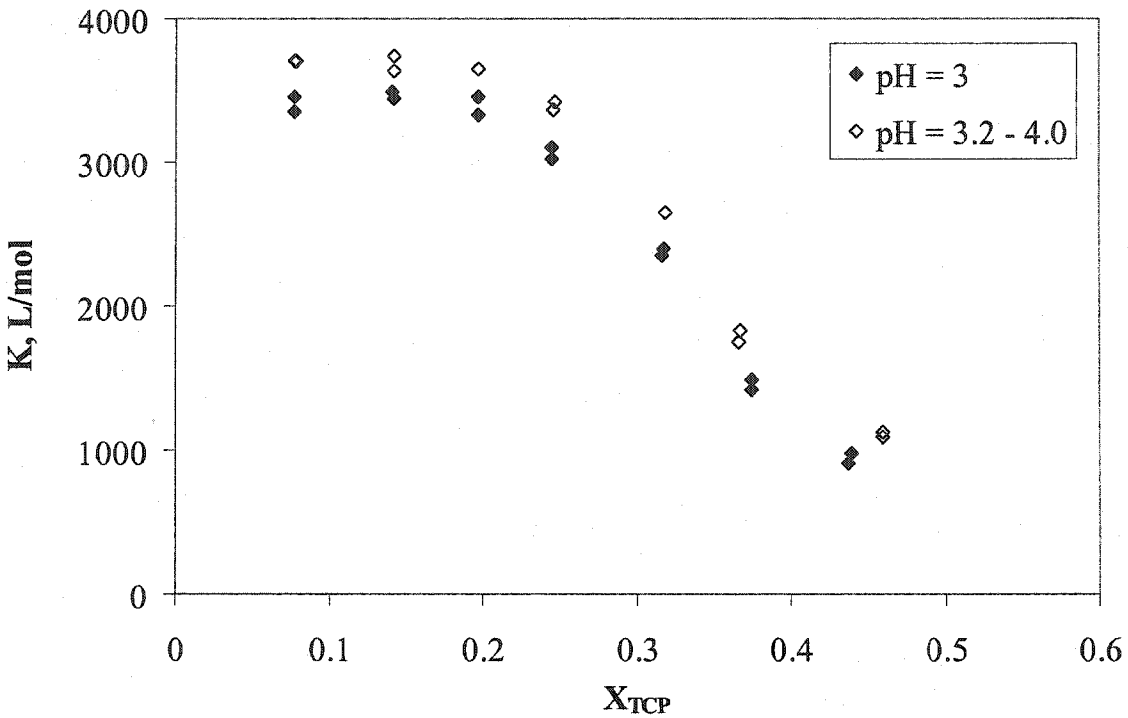


Figure 4. 7 Solubilization equilibrium constant of TCP vs mole fraction of TCP in CPC micelles. Initial [CPC] is 25 mM. Initial [NaCl] is 0 M.

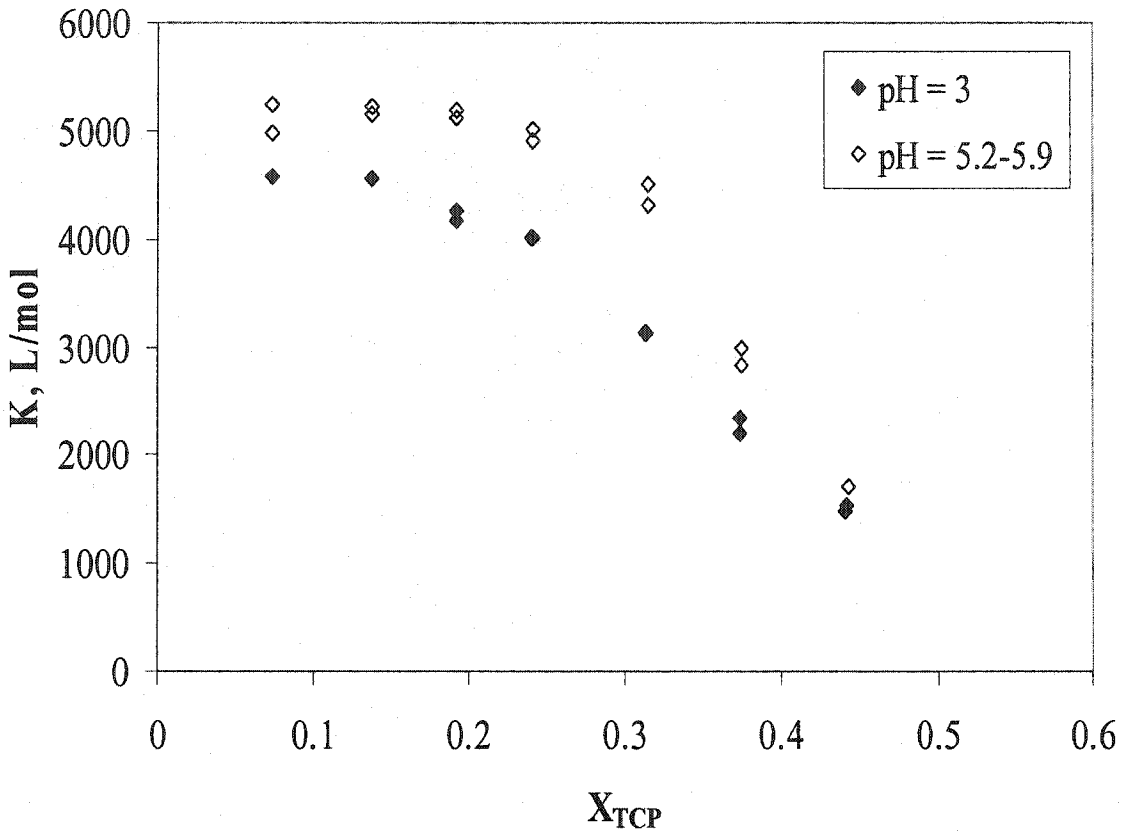


Figure 4. 8 Solubilization equilibrium constant of TCP vs mole fraction of TCP in CPC micelles. Initial [CPC] is 25 mM. Initial [NaCl] is 0.05 M.

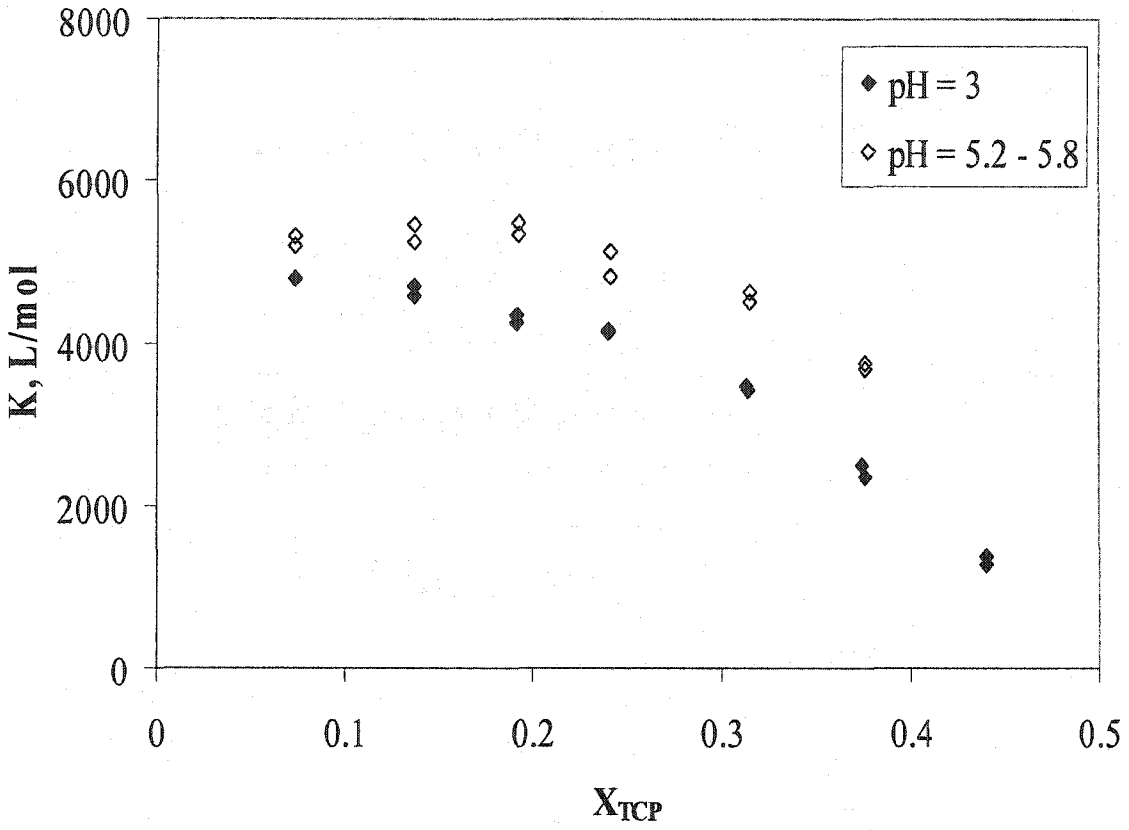


Figure 4. 9 Solubilization equilibrium constant of TCP vs mole fraction of TCP in CPC micelles. Initial [CPC] is 25 mM. Initial [NaCl] is 0.1 M.

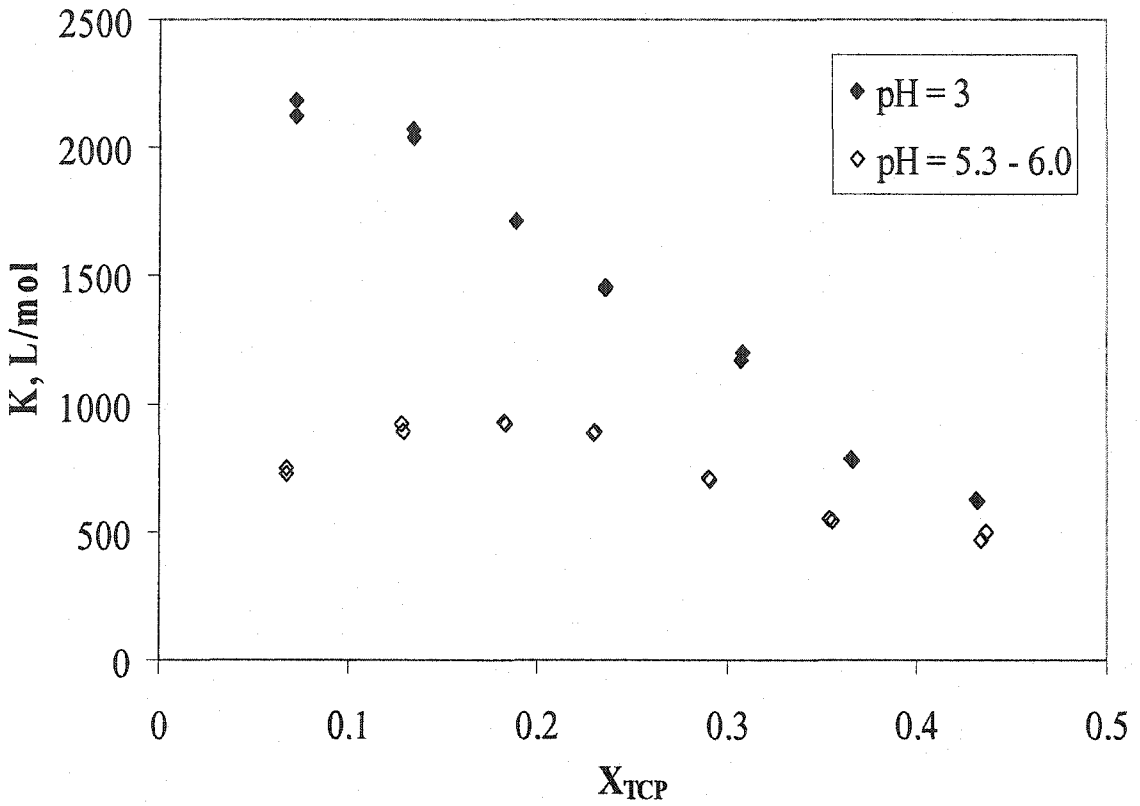


Figure 4. 10 Solubilization equilibrium constant of TCP vs mole fraction of TCP in CPC - PSS mixtures. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively. Initial [NaCl] is 0 M.

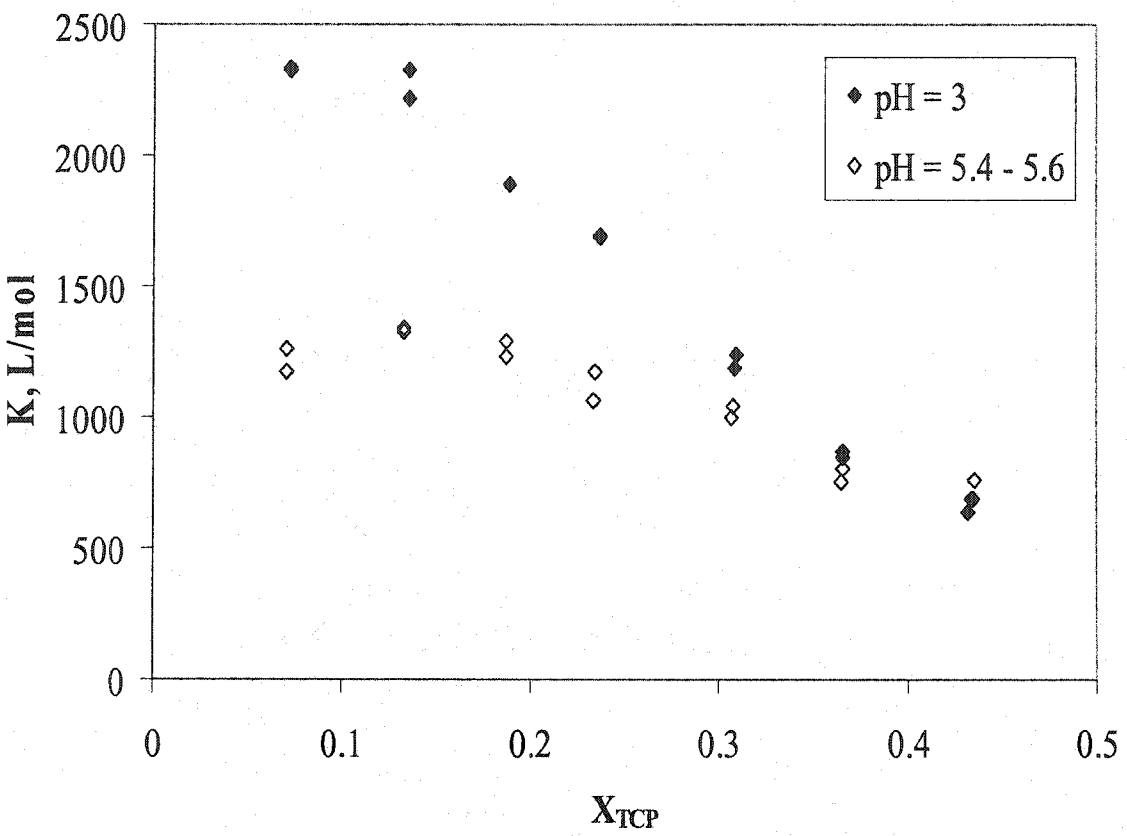


Figure 4. 11 Solubilization equilibrium constant of TCP vs mole fraction of TCP in the CPC - PSS mixtures. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively. Initial [NaCl] is 0.05 M.

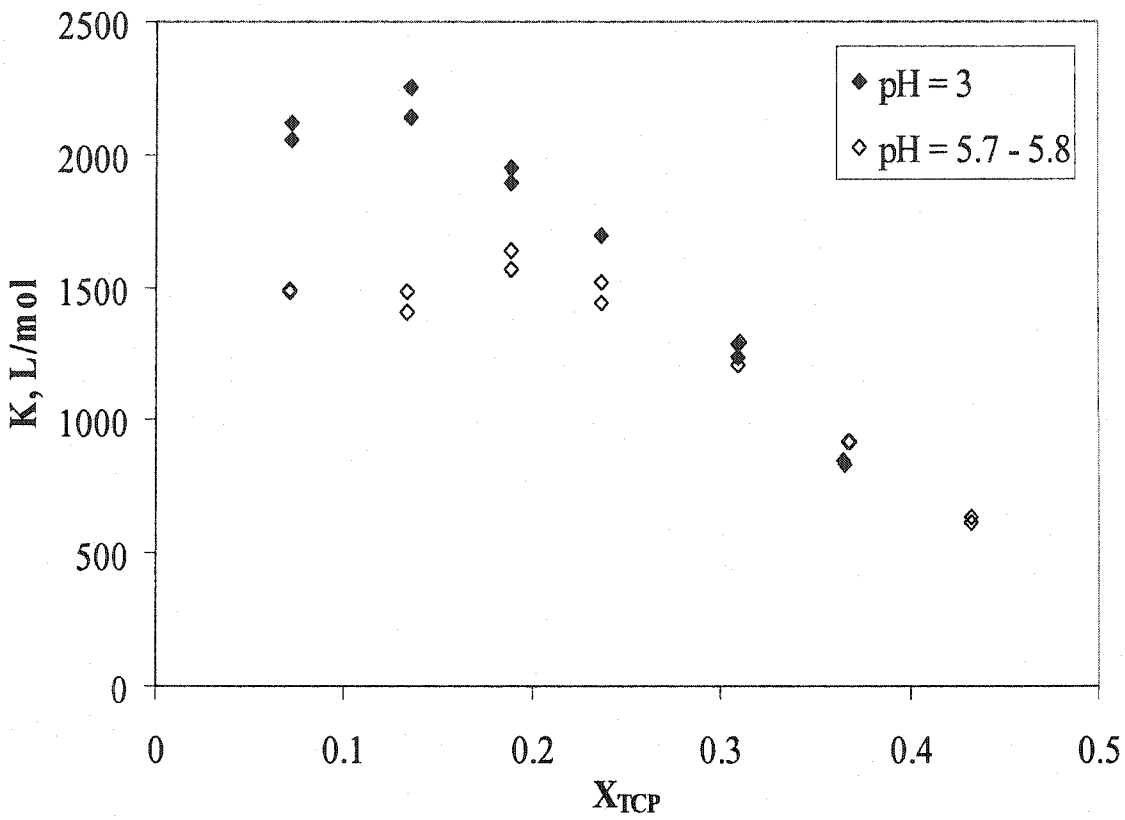


Figure 4. 12 Solubilization equilibrium constant of TCP vs mole fraction of TCP in the CPC - PSS mixtures. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively. Initial [NaCl] is 0.1 M.

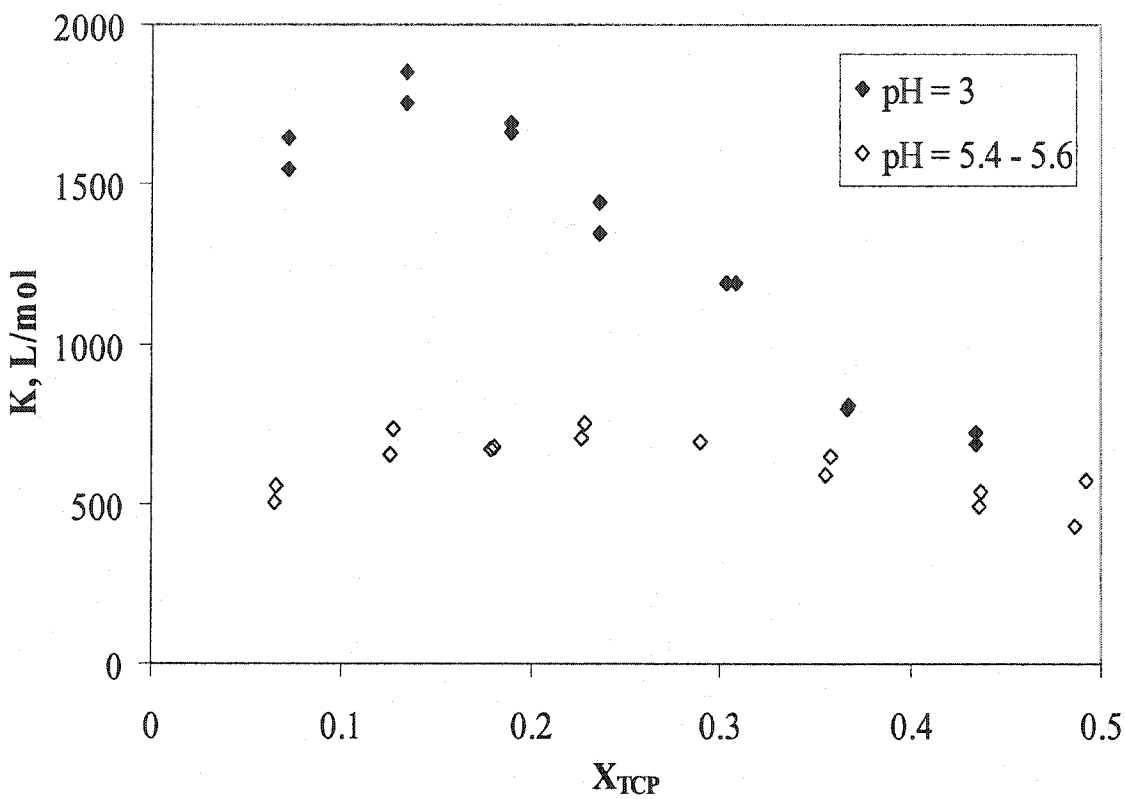


Figure 4. 13 Solubilization equilibrium constant of TCP vs mole fraction of TCP in the CPC - PSS mixtures. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively. Initial [NaCl] is 0 M.

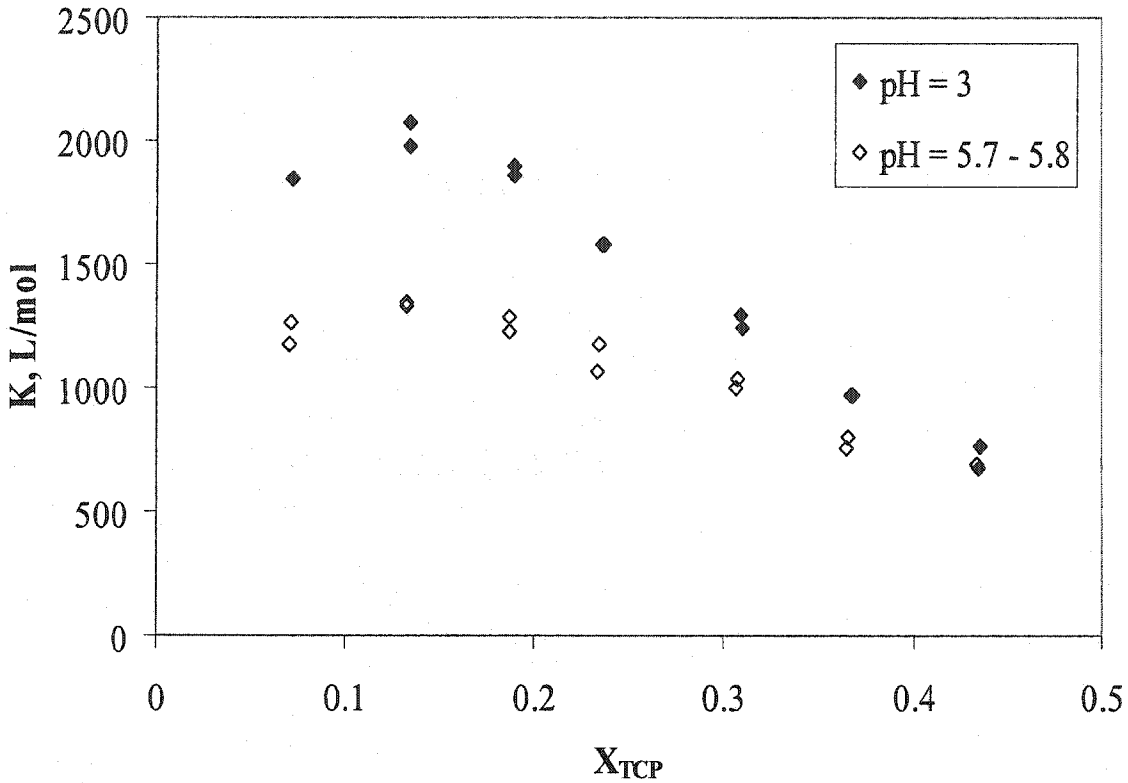


Figure 4. 14 Solubilization equilibrium constant of TCP vs mole fraction of TCP in the CPC - PSS mixtures. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively. Initial [NaCl] is 0.05 M.

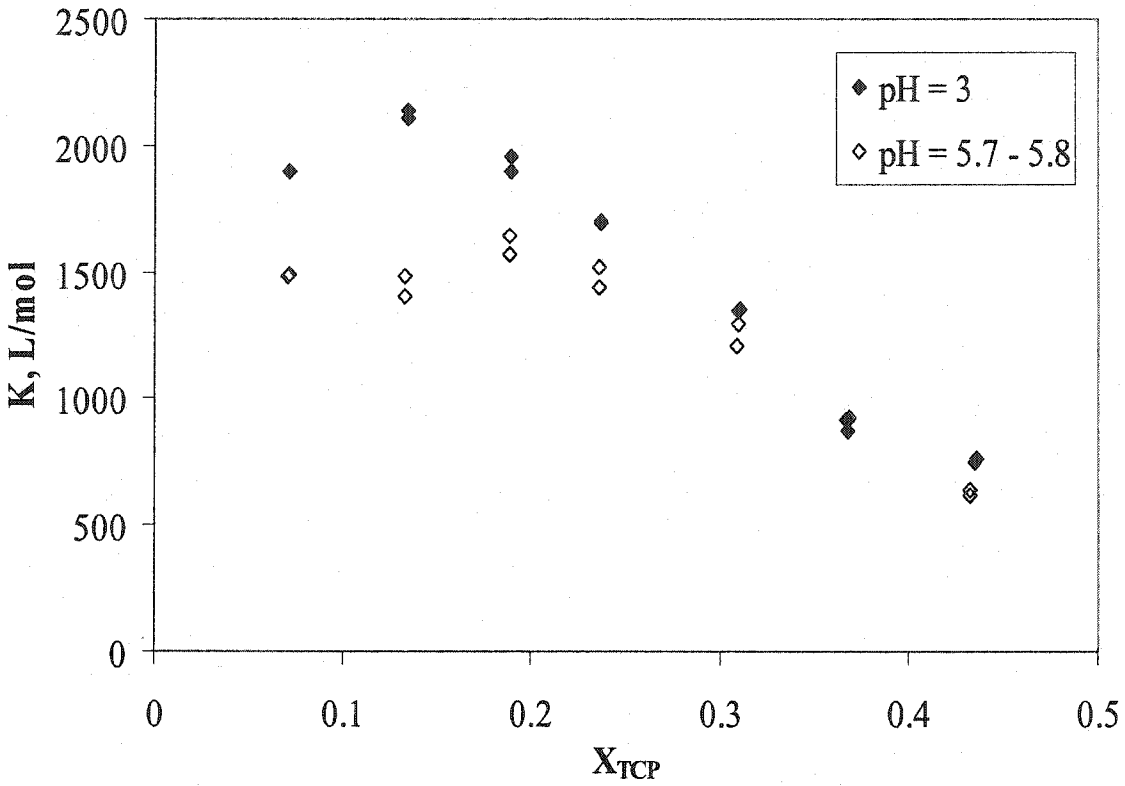


Figure 4. 15 Solubilization equilibrium constant of TCP vs mole fraction of TCP in the CPC - PSS mixtures. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively. Initial [NaCl] is 0.1 M.

CHAPTER 5

COLLOID-ENHANCED ULTRAFILTRATION OF CHLOROPHENOLS IN WASTEWATER: PART 2. EFFECT OF ADDED SALT ON SOLUBILIZATION IN SURFACTANT SOLUTIONS AND SURFACTANT-POLYMER MIXTURES

5.1 Abstract

The solubilization of three phenolic solutes in micellar solutions and surfactant - polymer mixtures is studied: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). Semiequilibrium dialysis (SED) is used to determine the solubilization equilibrium constant as a function of added NaCl concentration. The added salt enhances the solubilization ability of surfactant micelles, but it only slightly affects the solubilization constant of surfactant - polymer aggregates. The solubilization constant for the surfactant-only systems is greater than that for the surfactant - polymer systems. In the micellar solution, the solute with a low water solubility shows a greater solubilization constant than the solute with a higher water solubility; the solubilization constant increases in the order MCP < DCP < TCP. However, in the surfactant - polymer mixtures, the solubilization constant of DCP and TCP reverses due to two opposing effects: ion-dipole interaction and water solubility or hydrophobicity. Understanding and quantifying this solubilization

phenomenon is crucial to optimization of the performance of colloid-enhanced ultrafiltration separation processes.

5.2 Introduction

Most of surfactant studied for use in micellar-enhanced ultrafiltration (MEUF) are roughly spherical; however, surfactant configurations depend on such factors as surfactant concentration and salinity. For example, rod-like micelles for cetylpyridinium chloride (CPC) can occur at 0.3 M CPC[172]. Aqueous polymer - surfactant mixtures are of much interest from both fundamental and technological viewpoints. They are encountered in several industrial applications such as pharmaceuticals, personal care product formulation, enhanced oil recovery, and detergency. Surfactant binding to polymers in aqueous solution has been investigated extensively[67-68,75-79,82,173-176]. The overall picture for interaction in surfactant - polymer systems is that when the surfactant concentration exceeds a critical aggregation concentration (cac), surfactant bound to polymer begins to form micelle-like aggregates. Increasing surfactant concentration leads to increasing surfactant - polymer binding, until the polymer becomes saturated. This occurs at a surfactant concentration which is called c_{sat}. Free micelles do not appear until the unbound surfactant concentration reaches the CMC of the surfactant[173].

In the presence of polymer, the surfactant is induced by forming a micelle-like aggregate with a hydrophobic region in which solubilized organic can reside. The

binding of ionic surfactants to polymer is a cooperative process due to strong electrostatic and hydrophobic interactions. As a result, forming micelle-like organized structures occurs even at concentrations more than 1 order of magnitude lower than the CMC of surfactant[79,174-176]. The surfactant - polymer complex has been described as "micelles on a string" or "beads on a necklace" in which the polymer chain connects micelle-like surfactant aggregates by wrapping around them[69,77-78,82]. A few studies have been done to compare the solubilization ability of surfactant micelles and surfactant - polymer complexes[42-45,173], primarily for phenolic solutes. It was found that ordinary micelles can solubilize an organic solute more efficiently than the surfactant - polymer complexes. This behavior may be attributed to a reduction in absolute value of the electrical potential at the surface of surfactant aggregates due to neutralization by the oppositely charged polymer.

The total amount of solubilization in different surfactant - polymer systems have been measured over the past few decades[42-45,96,177-179]. Ikeda and Maruyama defined the (macroscopic) solubilization power as the number of molecules solubilized per molecule of micellized surfactant[179]. The (microscopic) solubilization capacity is defined as the average number of molecules solubilized in a single micelle at saturation. However, we use the more commonly utilized solubilization constant (K_A) which is expressed as mole fraction of solubilized solute into micelles (X_A) divided by unsolubilized solute concentration (c)[42-45]. Solubilization in micelles has been widely studied[180] whereas solubilization into surfactant - polymer complexes has received much less attention. In surfactant - polymer complexes, for surfactant concentrations

between cac and c_{sat}, all solubilization occurs in polymer-bound aggregates, while at concentrations where the unbound surfactant concentration reaches the CMC, both polymer-bound aggregates and free micelles participate in solubilization[173].

Organic solutes can solubilize at different locations in the micelle[112]. Polar solutes solubilize at the micellar surface or the palisade region whereas aliphatic hydrocarbons, such as hexane, solubilize primarily within the hydrocarbon core region of the micelles[51,112]. Since chlorine atoms are hydrophobic, for chlorinated phenols, the hydroxyl groups are located next to the cationic surfactant head groups due to ion-dipole interaction while the benzene ring is inserted into the hydrophobic interior of the micelles[112]. The solubilization ability of surfactant micelles and surfactant - polymer aggregates greatly depends on the solute characteristics such as hydrophobicity, water solubility and polarity. Solutes with a higher acidity (lower dissociation constant or pK_a) and lower water solubility can be solubilized more effectively than solutes with a low acidity and high water solubility, primarily with cationic surfactants[42,45-46,112,116,181]. This behavior can be seen in micellar-enhanced ultrafiltration (MEUF) and polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF) systems. In surfactant - polymer systems, two driving forces may influence the solubilization constant of neutral species solutes that have high hydrophobicity or low water solubility such as dichlorophenol (DCP) and trichlorophenol (TCP): ion-dipole interaction and hydrophobicity or water solubility. It was found that the ion-dipole interaction is dominant at low solute loading. Therefore, the surfactant - polymer aggregates can solubilize DCP more strongly than TCP[42] due to the greater

dipole moment of DCP than TCP[139]. At high solute concentration, the water solubility of solutes plays a more important role than the ion-dipole interaction; thus TCP has a higher solubilization constant than DCP[42].

For ionizable polar organic solutes such as chlorophenols; pH influences solute charge. When the pH is much higher than the pK_a of the solute, the phenolate anion predominantly exists in solution. It was found that the partition coefficient of the phenolate anion in a cationic surfactant micelle is higher than that of the neutral species because the interaction between the cationic surfactant head groups and the oppositely charged solute enhances the partition coefficients[148-149,181-182]. Therefore, the solubilization constant of the phenolate solute in the micellar solution is higher than that of the neutral species[181]. In contrast, the solubilization constant of the neutral species in surfactant - polymer aggregates is higher than that of the phenolate anion.

The effect of added simple salt on micellar growth has been investigated by several research groups[68,164-165,167-168,183-184]. The large impact of salt concentration on micellar size is commonly known; the micellar size increases as salt concentration increases. It was also found that the addition of salt increases the solubilizing power of surfactants[185-186], increases the surfactant aggregation number, and reduces the CMC[173]. In surfactant - polymer complexes, the added salt generally affects the surfactant binding. An increase of the ionic strength of solution shifts the onset of binding toward higher free surfactant concentrations and decreases the amount of bound surfactant[68]. These observations can be related to the screening influence of the simple salt, which acts to diminish the electrostatic interactions between surfactant

cations and polyanions[69,75]. Kim and coworkers found that at a given ionic strength, the aggregation number of a polymer-bound aggregate is approximately 50-60% smaller than that of a free micelle, while its solubilization ability is within approximately 20% of a free micelle[173].

Colloid-Enhanced ultrafiltration (CEUF) is the class of separation methods which include MEUF and PE-MEUF and can be used to remove dissolved organic solutes and/or inorganic ionic species from water[42,44,13-26]. Solubilization of organic solutes into micelles or surfactant - polymer complexes is the mechanism by which MEUF and PE-MEUF effect the separation[42].

The main objective of this paper is to investigate the effect of added salt on the solubilization ability of surfactant micelles and surfactant - polymer aggregates. Chlorophenolic solutes with different degrees of chlorination are chosen as our model to additionally investigate the effect of hydrophobicity of solute on solubilization constant in the presence of salt for an important class of wastewater pollutants, primarily in the pulp and paper industry. The organic solute concentration in the permeate is approximately equal to the unsolubilized solute concentration in the retentate[15-18]. Therefore, rejection in the ultrafiltration operation can be predicted from equilibrium solubilization constants and hence, this is the parameter that we measure in this work.

5.3 Experimental

As mentioned previously, the solubilization constant can be obtained using semiequilibrium dialysis (SED) experiment. A detailed description of the materials and methods used here is given in previous chapters.

5.4 Results and Discussion

5.4.1 Effect of Added Salt on Solubilization Constant

The solubilization equilibrium constant (K) of a solute A in CPC micelle or CPC - PSS aggregates can be determined as described previously (section 3.4). Most solubilization experiments were done without pH adjustment unless it is mentioned otherwise (i.e. Figs. 5.7 and 5.8); though the pH of the initial and final retentate solutions was recorded as shown in previous chapter (Tables 4.2 and 4.3, respectively). The reason that pH was not adjusted for higher pH conditions is that the addition of sodium hydroxide (NaOH) causes surfactant degradation. The percentage of the phenolate anion at the lowest solute concentration in the colloid solutions and at pH 3 is shown in Table 4.4. This is to make a comparison of the solubilization constants of TCP between two different systems, one of which is the system containing a mixture of neutral species and charged species (system without pH adjustment) and the other is the system predominantly containing neutral species

(system at pH 3) except the micellar system in the absence of salt that contains 11% phenolate anion. However, as shown in Table 4.4, the system at higher pH contains greater percentage of the phenolate anion, as compared to the system at lower pH.

As shown in Figs. 5.1 through 5.8, the solubilization equilibrium constants (K_A) obtained by SED experiments for MCP, DCP, and TCP are plotted as a function of intramicellar mole fraction (X_A) of the solutes in CPC micelles and CPC - PSS complexes at different salinities. The pH range in the final retentate solutions is shown in parenthesis in the figures. From Figs. 5.1 through 5.3, it can be seen that the solubilization constant of CPC micelles in the presence of salt is higher than that in the absence of salt and as also seen in the system at pH 3 (Fig. 5.7). In the presence of 50 mM PSS, the added salt does not significantly affect the solubilization ability of CPC - PSS complexes for MCP and DCP, as shown in Figs. 5.4 and 5.5. However, K_{TCP} increases with increasing salinity for the system without pH adjustment (Fig. 5.6) and at pH 3 (Fig. 5.8).

It is well-known that micellar growth occurs as the electrolyte concentration increases[167-168,183-184]. This is attributed to the fact that the initial added salt reduces the electrostatic repulsion between surfactant head groups, and therefore increases the micellar size and the surfactant aggregation number. The increase in the micellar size could cause the increase in the solubilization ability of the micelle as salt concentration increases, as seen in Figs. 5.1 through 5.3 and Fig. 5.7. However, the further addition of salt may not significantly change the micellar size, resulting in only a slight or negligible increase in the solubilization constant when the salt concentration

is increased from 0.05 M to 0.1 M. The increase in the solubilization constant may be partly due to a salting-out effect which causes a reduction in water solubility of the organic solutes in the aqueous solution[183], and therefore enhances the solubilization ability of the CPC micelle. A previous study[181] showed that the apparent pK_a of chlorophenolic solutes in micellar solution increases as [NaCl] increases. This suggests that the solutes become less ionizable or have less water solubility. It should be noted that the micellar system without salt contains the phenolate anion in a greater percentage as compared to the system with salt, as shown in Table 4.4; this might lead to an increase in the solubilization constant in the absence of salt due to the ion-ion interaction between the phenolate anion and the surfactant head groups. However, the effect of the micellar size may play a stronger role than the effect of the phenolate anion. In addition to the effect of added salt, a synergistic effect of organic solute on the micellar growth has been observed[183-184].

In the surfactant - polymer mixtures, it is commonly known that the size and the aggregation number of surfactant - polymer aggregates are smaller than those of ordinary micelles[74,176,187]. Kogej and coworkers reported the characteristic size of the ordered element ($\bar{a}$) of CPC - PSS[82]; the $\bar{a}$ value is the center-to-center distance between micelles consecutively bound to the polyion, which comprises one micellar diameter and the thickness of the polymer chain wrapped around it. They found that the $\bar{a}$ value is approximately 35.2-38.0 Angstroms which is less than the largest possible extension of two C_{16} hydrocarbon chains incorporated in a liquid hydrocarbon-like environment. It should be noted that the length of a fully extended

cetyl (C_{16}) chain approximately is 21.74 Angstroms [58]; therefore, the largest possible extension of two C_{16} hydrocarbon chains, or the diameter of a micelle not taking the head groups into account is $43.5\,A°$. Hansson and Almgren found that the aggregation numbers of surfactant - polymer aggregates are not significantly affected by the presence of salt[74] This suggests that the aggregate size may not be drastically influenced by the added salt, which may explain that the solubilization ability of the surfactant - polymer aggregates is not dramatically affected by the added salt for MCP, DCP, and TCP at pH 3. It should also be noted that there are only negligible concentrations of charged species present for MCP, DCP and TCP at pH 3. In addition, the counterions present in the surfactant - polymer mixtures, at a relatively higher concentration than in the surfactant solutions, have already diminished the electrostatic repulsion between surfactant head groups. Therefore, additional salt may no longer affect the electrostatic repulsion, and consequently the size or the aggregation number of the surfactant - polymer aggregates. In addition, the polymer-bound micelles are partly neutralized by the polyanion and have therefore lower charge density than the corresponding free ones. This feature also entails that the polymer-bound micelles are less affected by an increases electrolyte concentration.

In the surfactant – polymer systems, the increase in the solubilization constant for TCP as the salt concentration increases, as shown by Fig. 5.6, is somewhat difficult to understand. The authors speculate that the presence of the phenolate anion could be a reason for such phenomena. Although the presence of the phenolate species (from the previous chapter) as shown in Table 4.4 can be negligible, the numbers in the table

were obtained at a low solute concentration of 0.3 mM. The presence of the phenolate anion can be higher at higher solute concentrations and thus influences the solubilization of TCP by the surfactant - polymer complexes.

5.4.2 Effect of Types of Colloid on Solubilization Constant

Figs. 5.9 through 5.11 show plots between the solubilization constant and intramicellar mole fraction of MCP, DCP, and TCP, which illustrates the effect of type of colloid in the presence of salt. It is observed that the solubilization constant in the micellar solution monotonically decreases as the solute concentration increases and is higher than the solubilization constant of surfactant - polymer aggregates. This behavior was also seen in a system without salt[42] (Chapter 3). The increase in polymer concentration from 50 mM to 75 mM does not significantly influence the solubilization constant in surfactant - polymer system although the solubilization constant of DCP at 50 mM PSS is slightly higher than the solubilization constant at 75 mM PSS as shown in Fig. 5.10. Results for the system with 0.1 M NaCl are approximately the same as the system with 0.05 M NaCl; therefore, the results at 0.1 M NaCl are not shown here. The solubilization of polar solutes in neutral form generally occurs at the micellar surface and palisade region with significant ion-dipole interaction[112,138]. The solubilization behavior has been observed to follow Langmuir adsorption isotherm. This suggests that the adsorption initially occurs at the micellar surface. The adsorption or the solubilization of the solutes decreases once all active

site are occupied as solute concentration increases as seen in the Figs. 5.9 through 5.11. This type of behavior was also observed in previous work[42,45-46,112,181]. Since TCP is relatively hydrophobic, the solubilization could take place in the palisade layer or/and the outer part the hydrophobic region, resulting in a constant solubilization at low solute loading, as shown in Fig. 5.11. Once the hydrophobic region and the palisade layer are filled up, the solubilization will take place at the micellar surface, which is indicated by the decrease in the solubilization constant as the solute loading increases.

The reduction of the solubilization constant in the presence of polymer may be attributed to the decrease in the charge density at the micellar surface due to the neutralization process of the surfactant by the polymer. In addition, as noted previously, the size of surfactant - polymer aggregate is smaller than the size of the ordinary micelle. As a result, the volume in the palisade layer is reduced, causing steric hindrance for the hydroxyl groups to penetrate there, therefore decreasing the solubilization constant.

5.4.3 Effect of Types of Solute on Solubilization Constant

The data is replotted to investigate the effect of type of solute on the solubilization constant of the surfactant micelle and the surfactant - polymer aggregates in the presence of 0.05 M and 0.1 M NaCl, as shown in Figs. 5.12 through 5.17. In the micellar solutions at both salt concentrations, the solubilization constant

of the solutes increases in the order MCP < DCP < TCP, as shown in Figs. 5.12 and 5.13. In the surfactant - polymer mixtures at 50 mM PSS, the solubilization constant of DCP and TCP is reversed at both salt concentrations, as shown in Figs. 5.14 and 5.15. The solubilization of DCP is higher than that of TCP at low solute loading whereas the opposite trend is observed at high solute loading as seen by the intersection between the solubilization isotherm for DCP and TCP. In the presence of 50 mM PSS, the intersection seems to occur at a lower solute loading when the salt concentration increases from 0.05 M (Fig. 5.14) to 0.1 M (Fig. 5.15). At 75 mM PSS, the intersection no longer exists at 0.1 M NaCl; the solubilization of the solutes at 0.1 M NaCl follows the same order found in the micellar systems.

In general, the lower the water solubility, the greater the solubilization constant because the solute with low water solubility tends to partition into surfactant micelle more effectively than the solute with high water solubility. It should be noted that the water solubility increases in the order TCP < DCP < MCP[136]. As seen in Figs. 5.12 and 5.13, the values of K for the solutes are in inverse order compared to water solubility for the micellar systems.

In the surfactant - polymer systems, the previous study showed that DCP and TCP were almost completely protonated under the conditions used here[181]. Therefore, ion-dipole interaction can affect the solubilization of the solute in the surfactant aggregate. The dipole moment (μ) of MCP, DCP, and TCP is reported as 2.93, 2.25, and 1.08 D, respectively[139], which has an opposite order to hydrophobicity of the solute or the same order as water solubility (e.g., TCP shows the greatest

hydrophobicity and the lowest water solubility). As a result, the two opposing effects of ion-dipole interaction and water solubility for a given solute are present as also seen in previous work[42]. As salt concentration increases from 0.05 M to 0.1 M, the effect of ion-dipole interaction on the solubilization constant may be diminished; therefore the intersection between the solubilization isotherm of DCP and TCP occurs at a lower solute concentration. Likewise, the ion-dipole interaction may be reduced as polymer concentration increases from 50 mM to 75 mM, resulting in the disappearance of the intersection point in Fig. 5.17 as compared to Fig. 5.15. In the presence of 75 mM PSS and 0.1 M NaCl, it is plausible that solubilization constant is predominantly affected by the water solubility; therefore the order of the solubilization constants is the same as the order observed in the micellar solution. The solubilization of MCP in both figures are smallest over an entire range of concentration because of its lower hydrophobicity or higher water solubility, compared to DCP and TCP, although its dipole moment is the greatest.

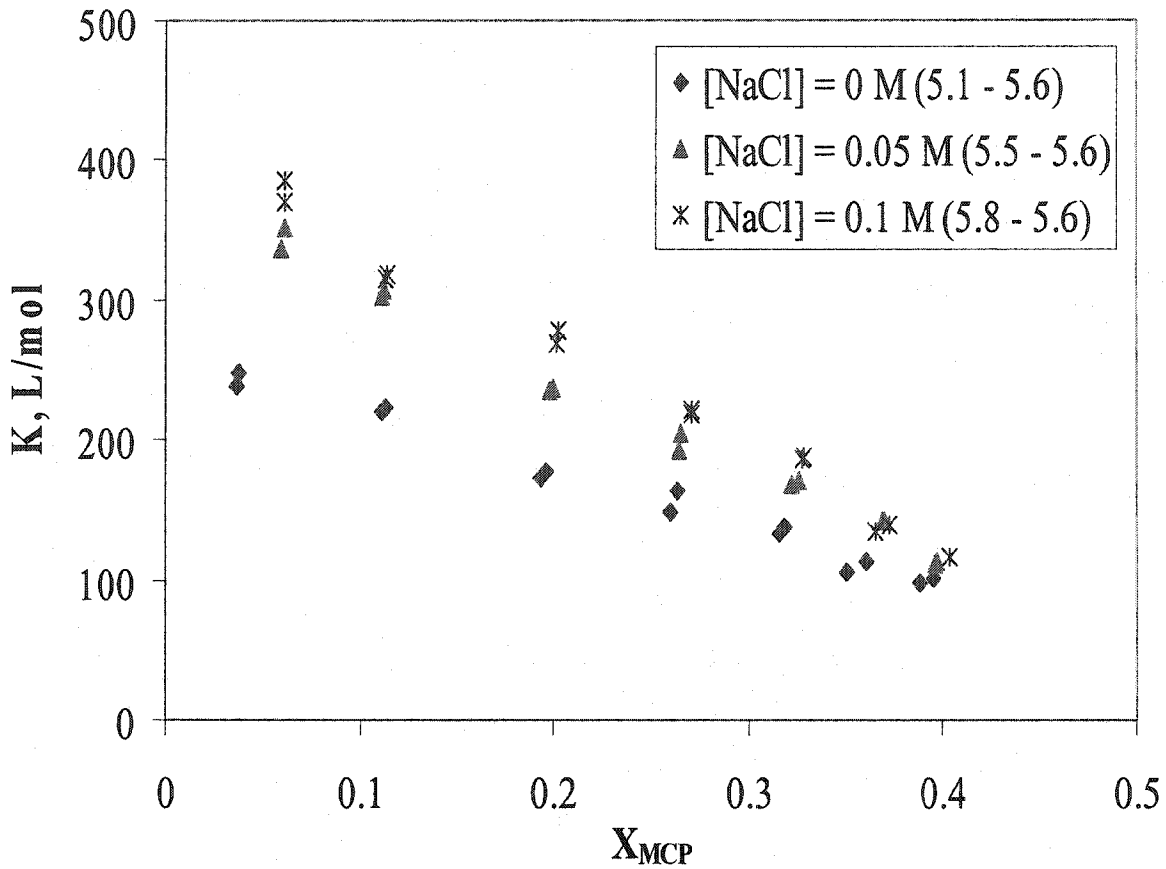


Figure 5. 1 Solubilization equilibrium constant of MCP vs mole fraction of MCP at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

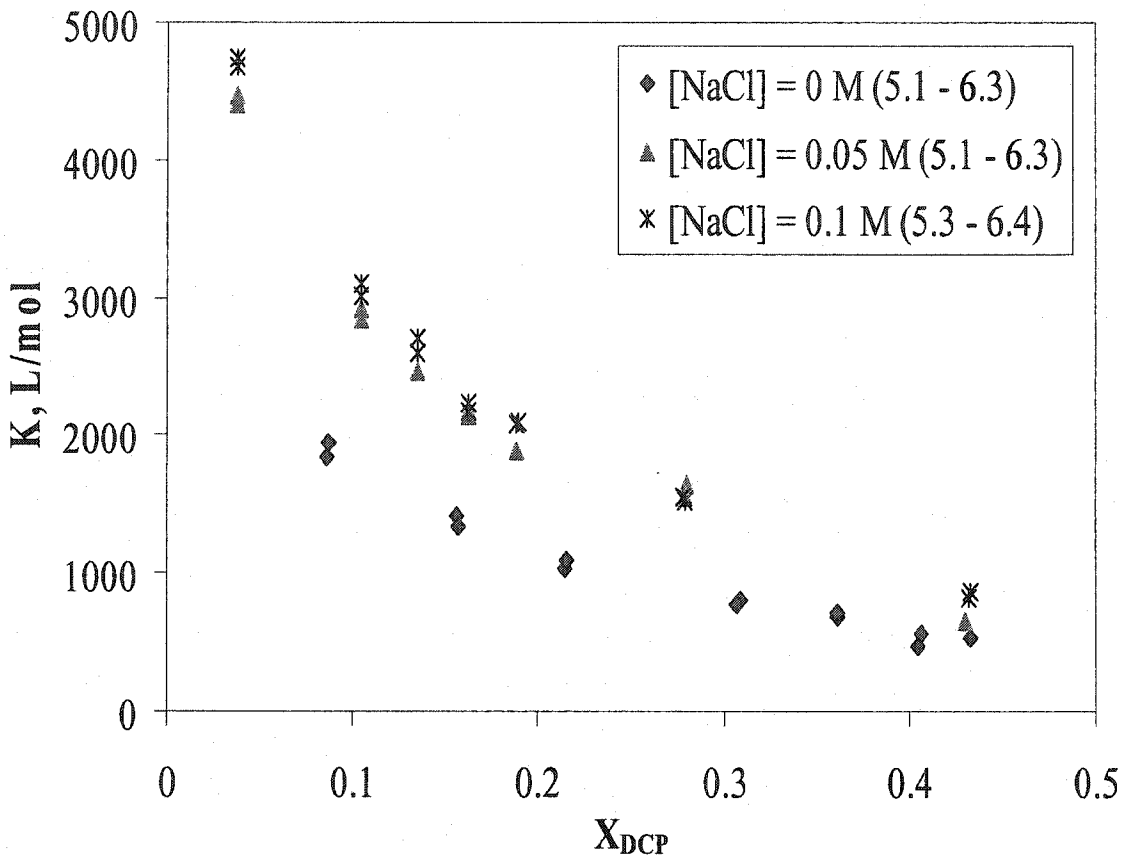


Figure 5. 2 Solubilization equilibrium constant of DCP vs mole fraction of DCP at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

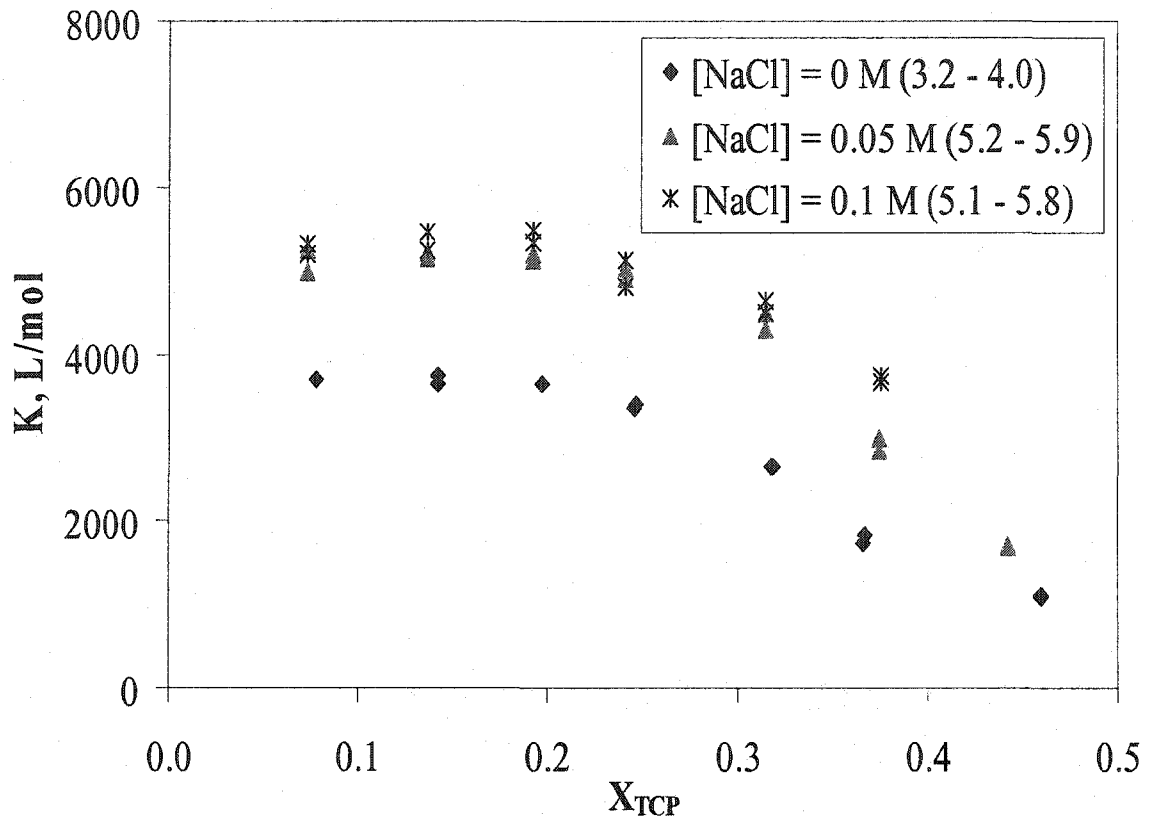


Figure 5. 3 Solubilization equilibrium constant of TCP vs mole fraction of TCP at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

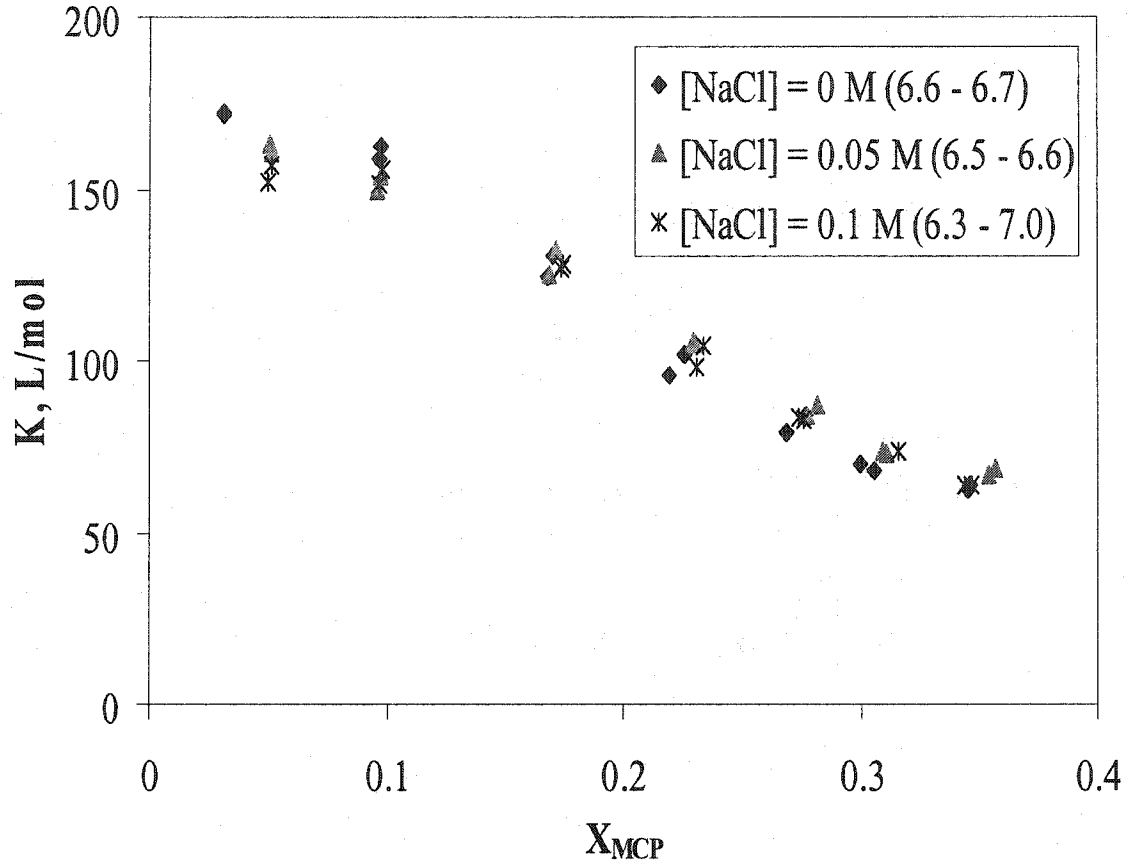


Figure 5. 4 Solubilization equilibrium constant of MCP vs mole fraction of MCP at different NaCl concentrations in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM to 50 mM, respectively.

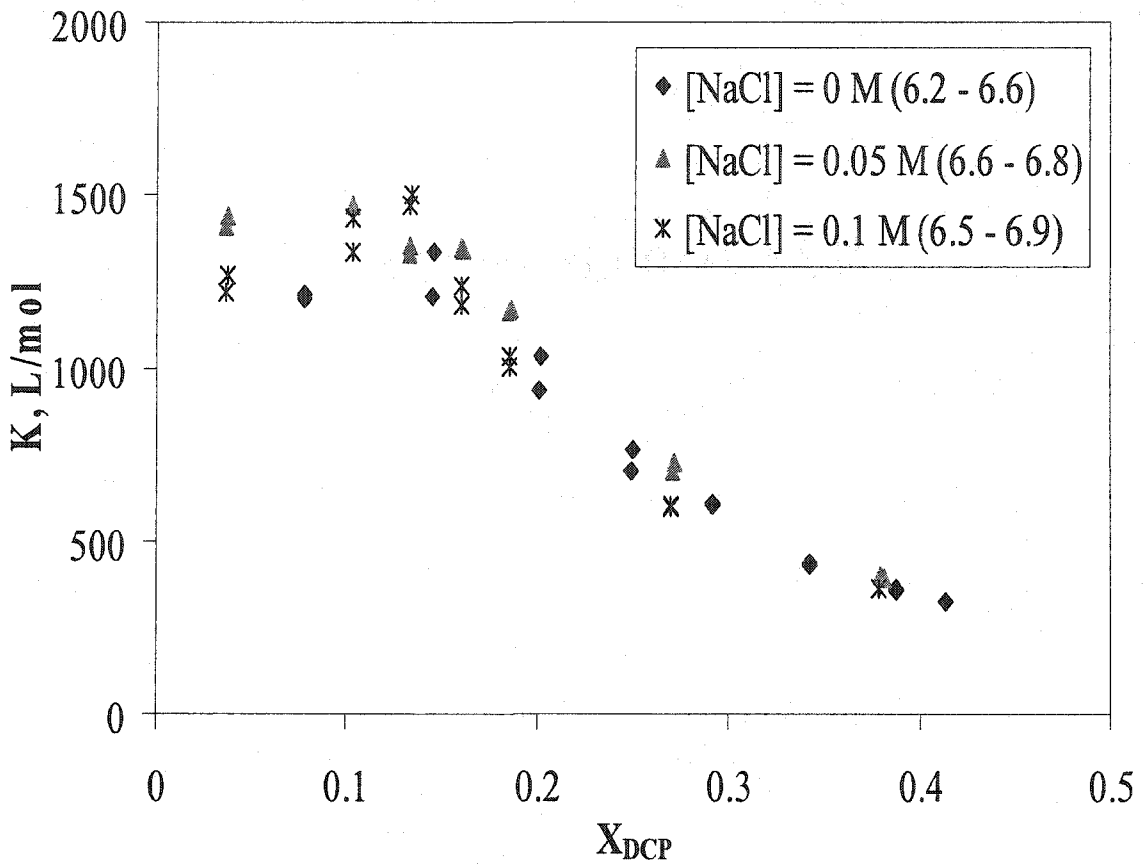


Figure 5. 5 Solubilization equilibrium constant of DCP vs mole fraction of DCP at different NaCl concentrations in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

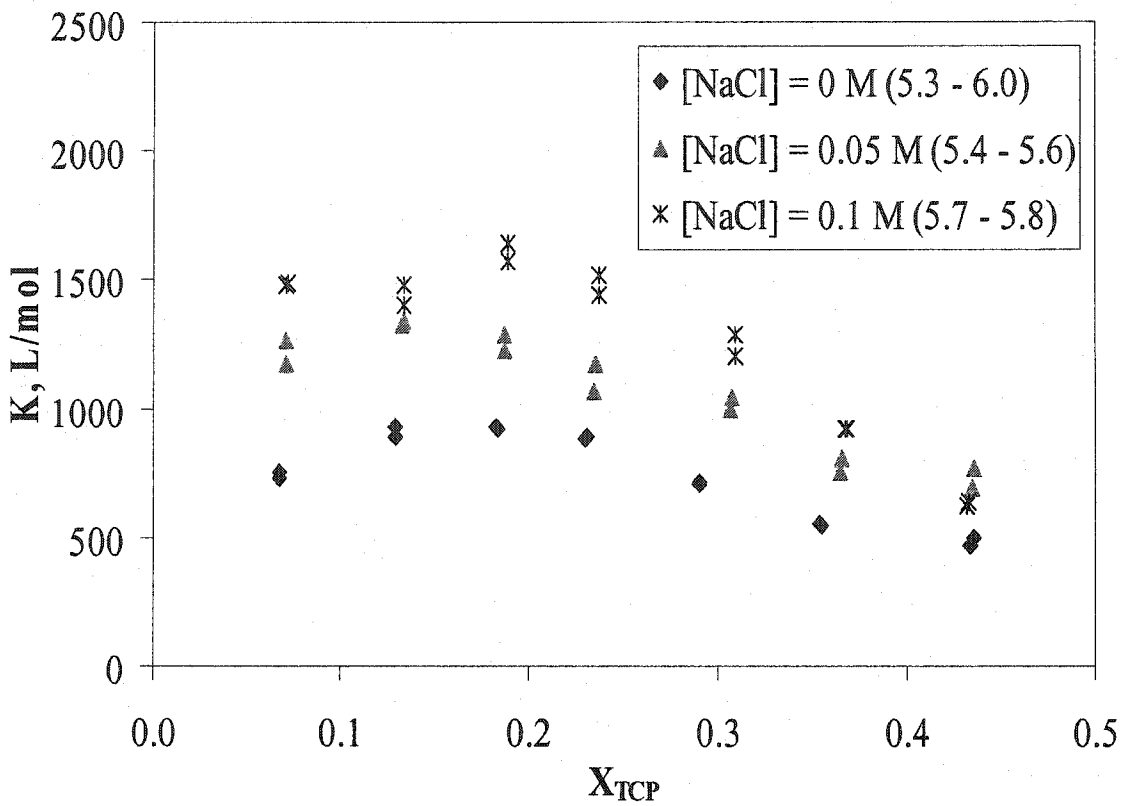


Figure 5. 6 Solubilization equilibrium constant of TCP vs mole raction of TCP at different NaCl concentrations in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 M, respectively.

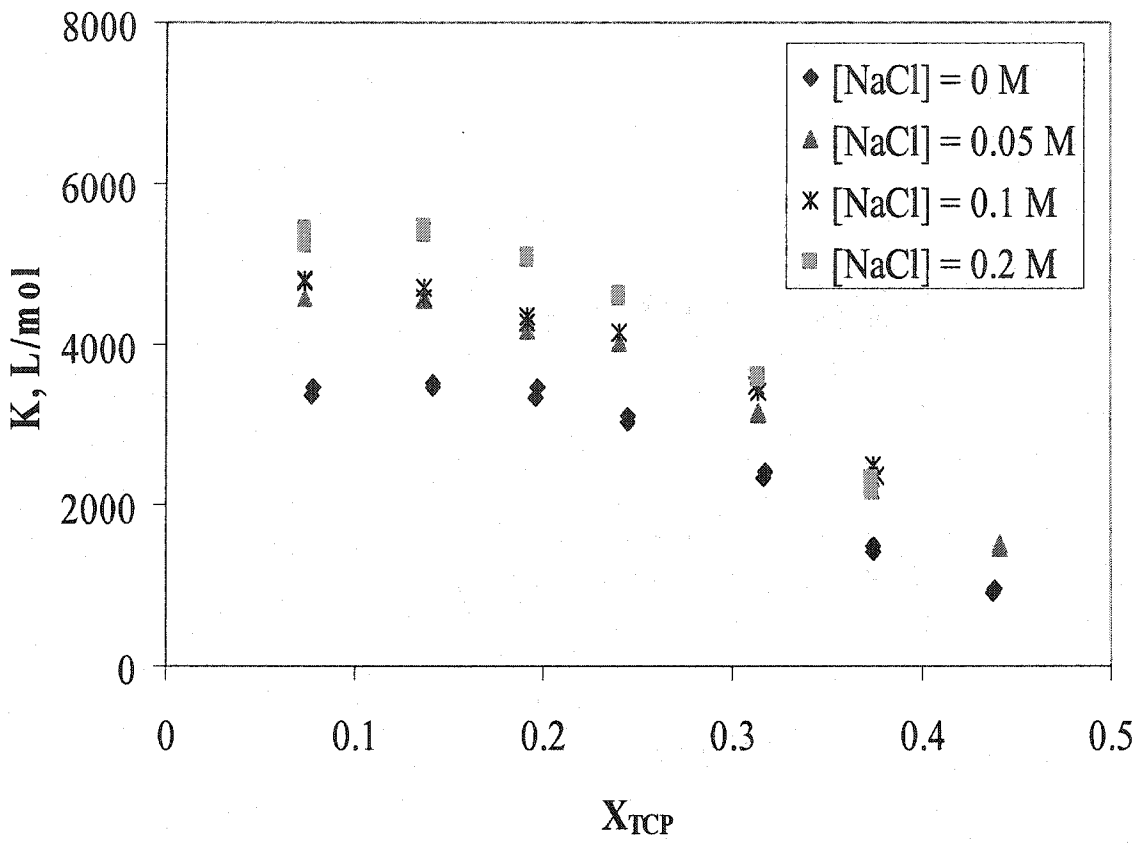


Figure 5. 7 Solubilization equilibrium constant of TCP vs mole fraction of TCP at different NaCl concentrations in CPC micelles at pH of 3. Initial [CPC] is 25 mM.

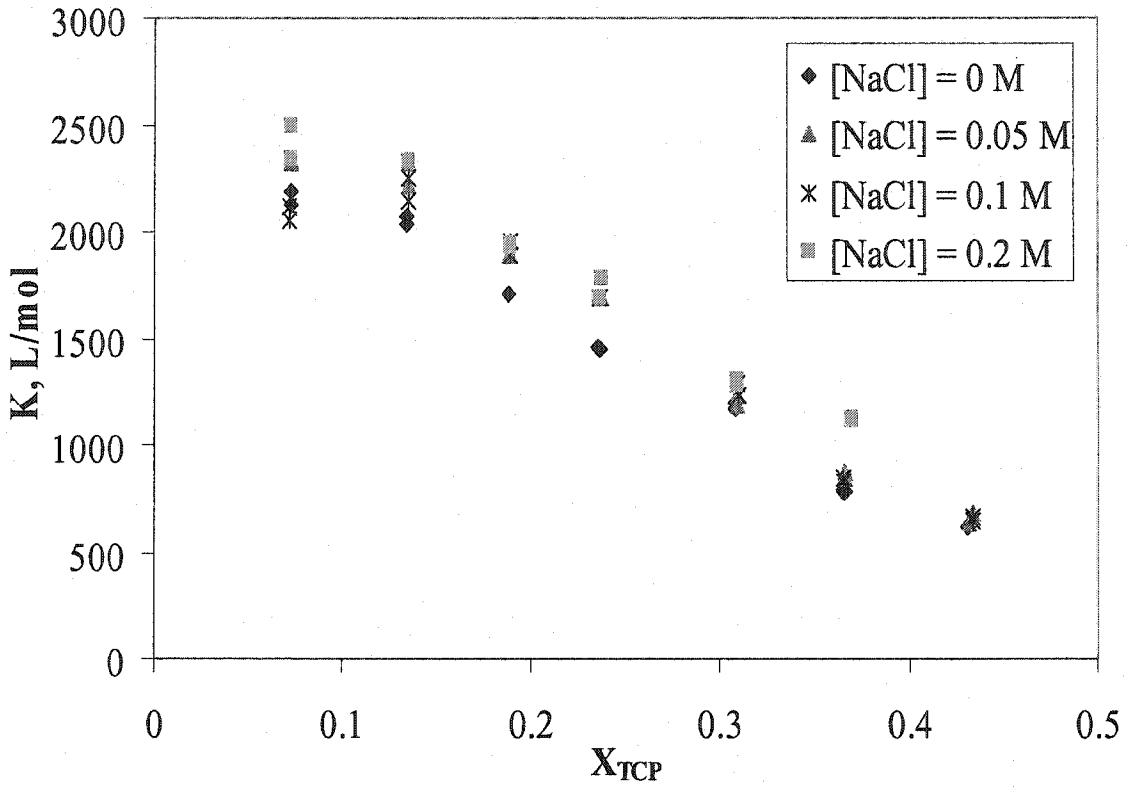


Figure 5. 8 Solubilization equilibrium constant of TCP vs mole fraction of TCP at different NaCl concentrations in CPC - PSS complexes at pH of 3. Intitial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

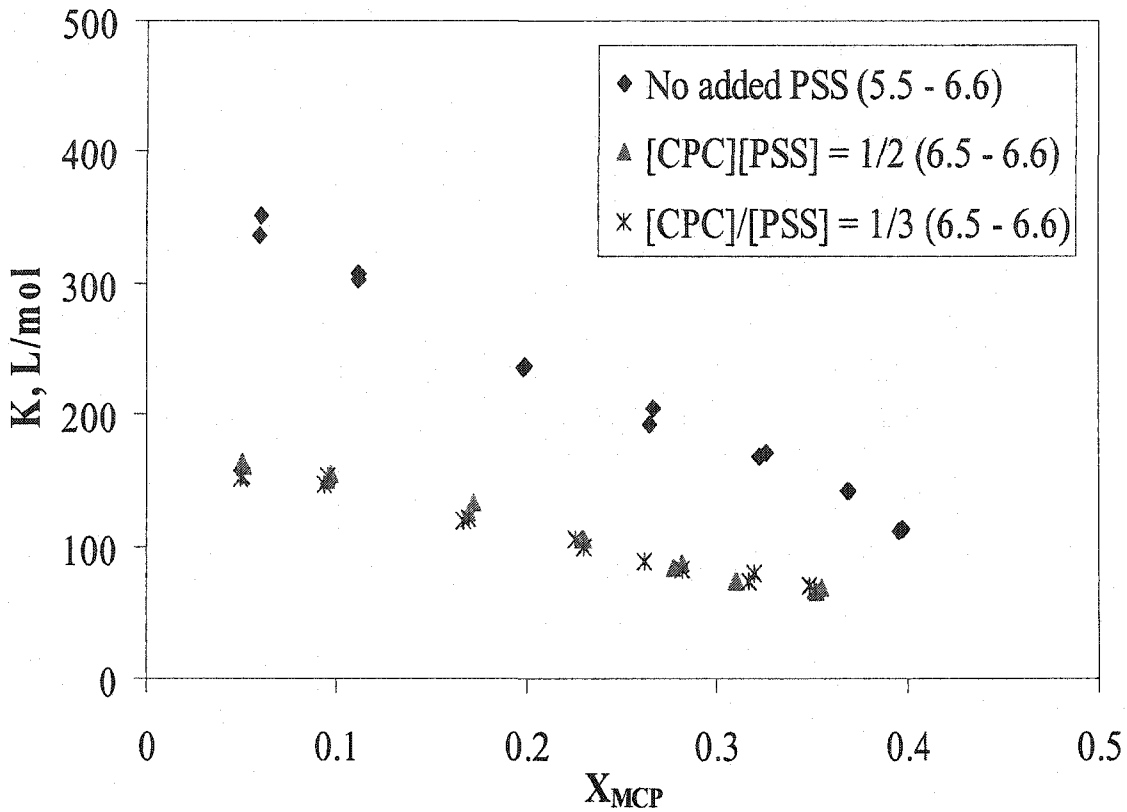


Figure 5. 9 Solubilization equilibrium constant of MCP vs mole fraction of MCP in different types of colloids. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ration 1:3). Initial [NaCl] is 0.05 mM.

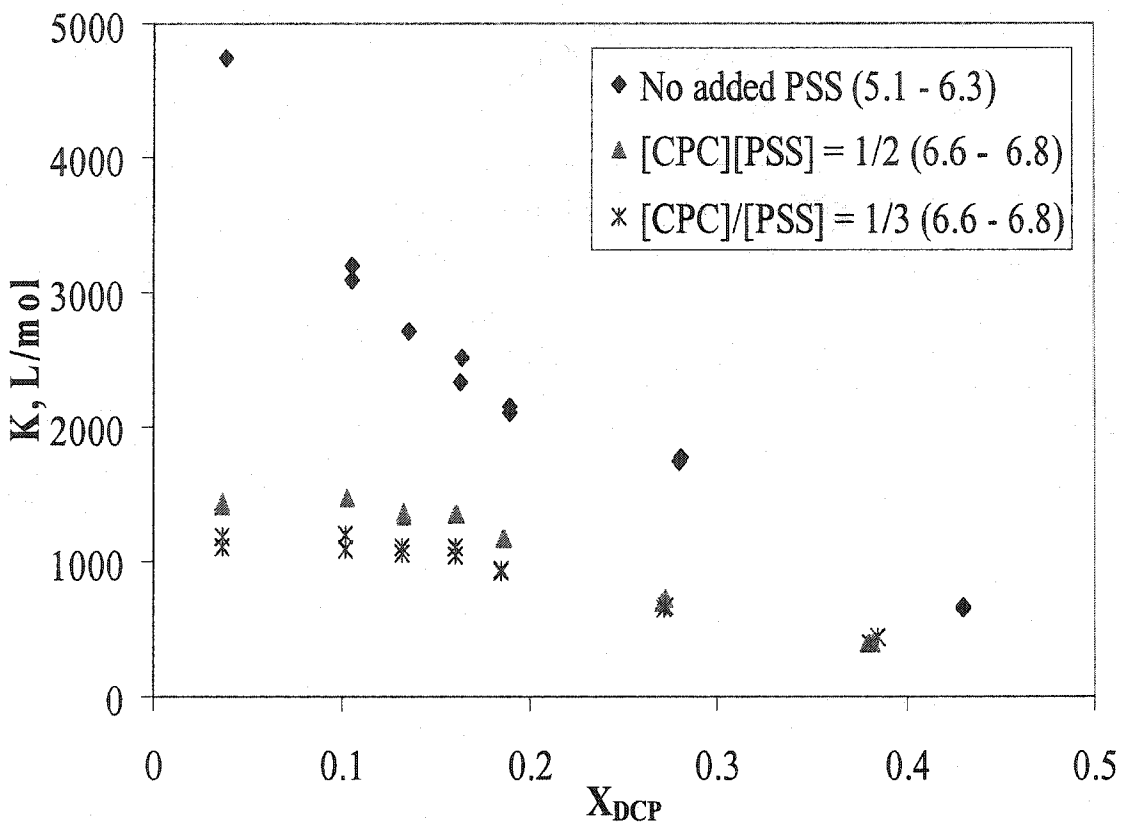


Figure 5. 10 Solubilization equilibrium constant of DCP vs mole fraction of DCP in different types of colloids. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ration 1:3). Initial [NaCl] is 0.05 mM.

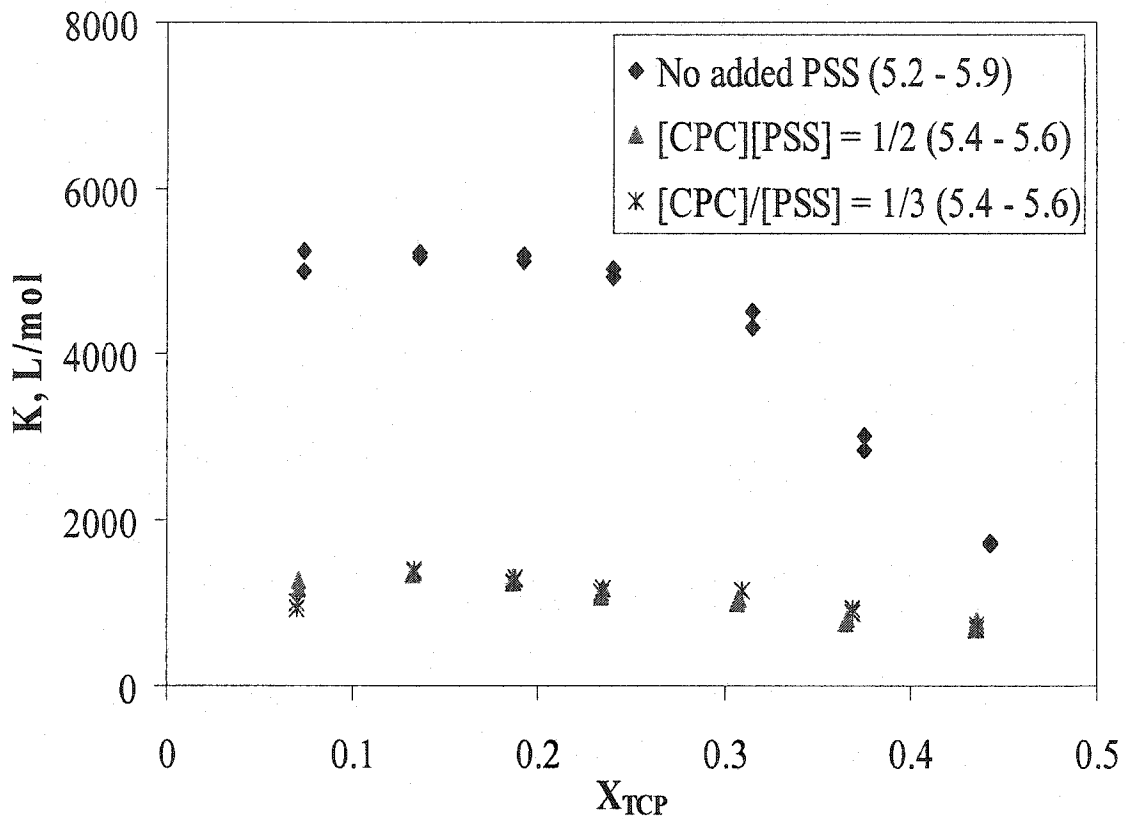


Figure 5. 11 Solubilization equilibrium constant of TCP vs mole fraction of TCP in different types of colloids. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3). Initial [NaCl] is 0.05 mM.

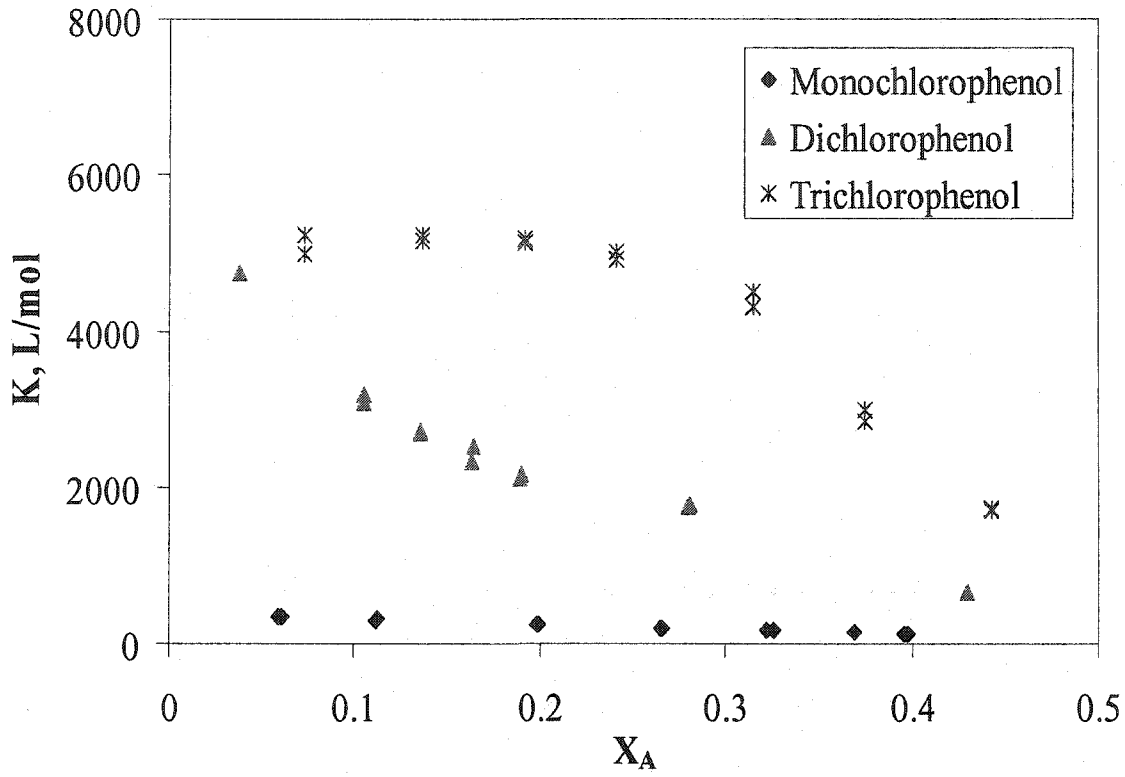


Figure 5. 12 Solubilization equilibrium constant vs mole fraction for different solutes in CPC micelle. Initial [CPC] is 25 mM. Initial [NaCl] is 0.05 M.

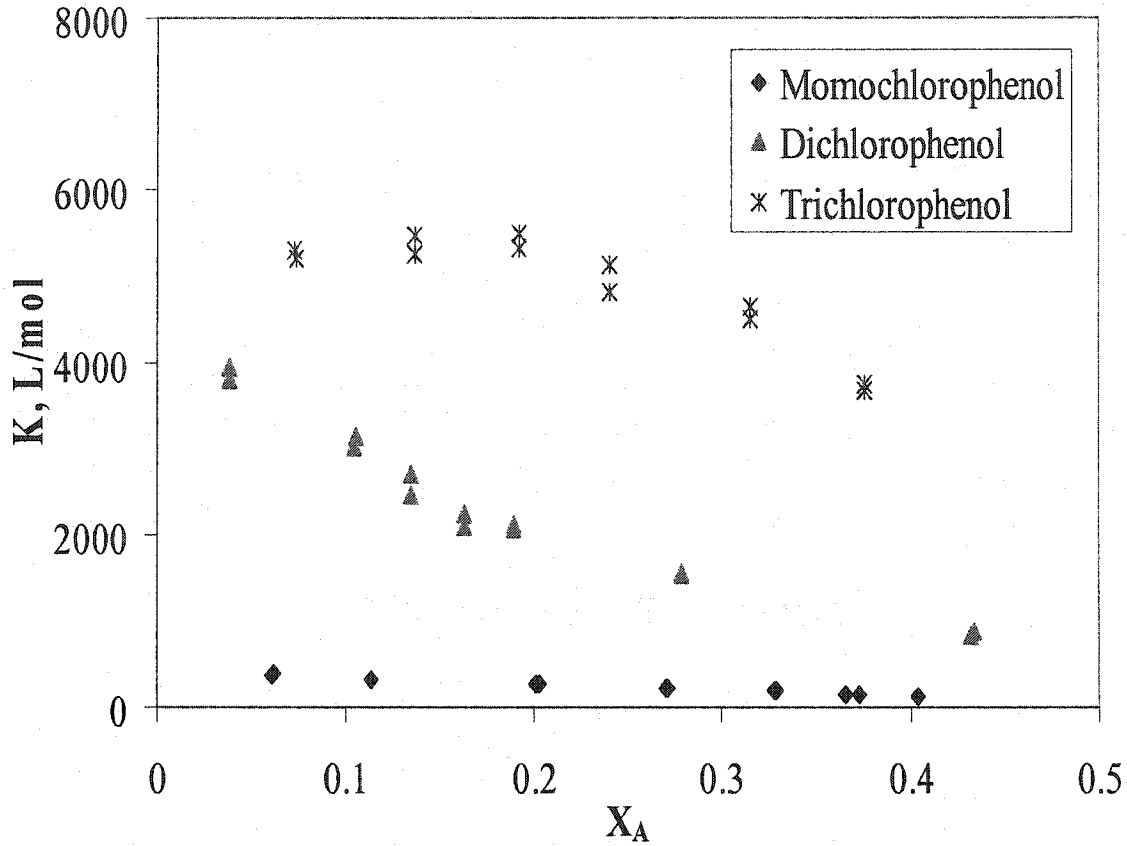


Figure 5. 13 Solubilization equilibrium constant vs mole fraction for different solutes in CPC micelle. Initial [CPC] is 25 mM. Initial [NaCl] is 0.1 M.

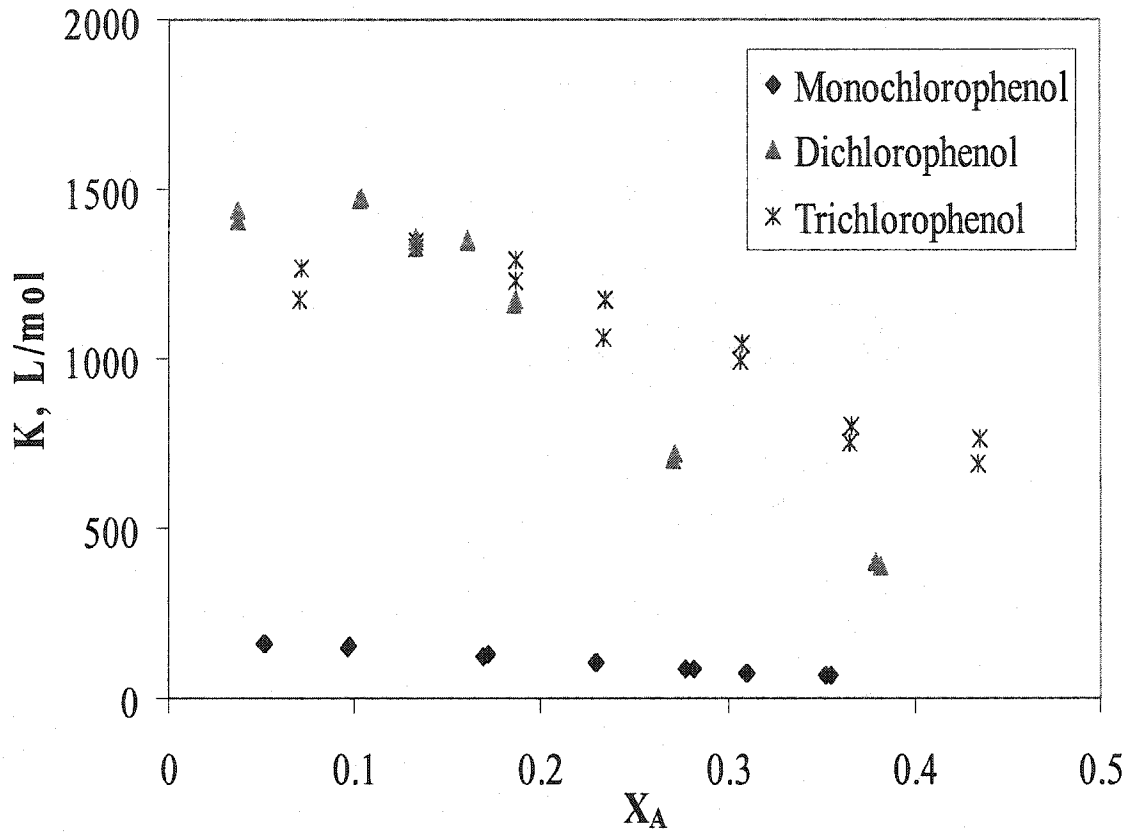


Figure 5. 14 Solubilization equilibrium constant vs mole fraction for different solutes in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively. Initial [NaCl] is 0.05 M.

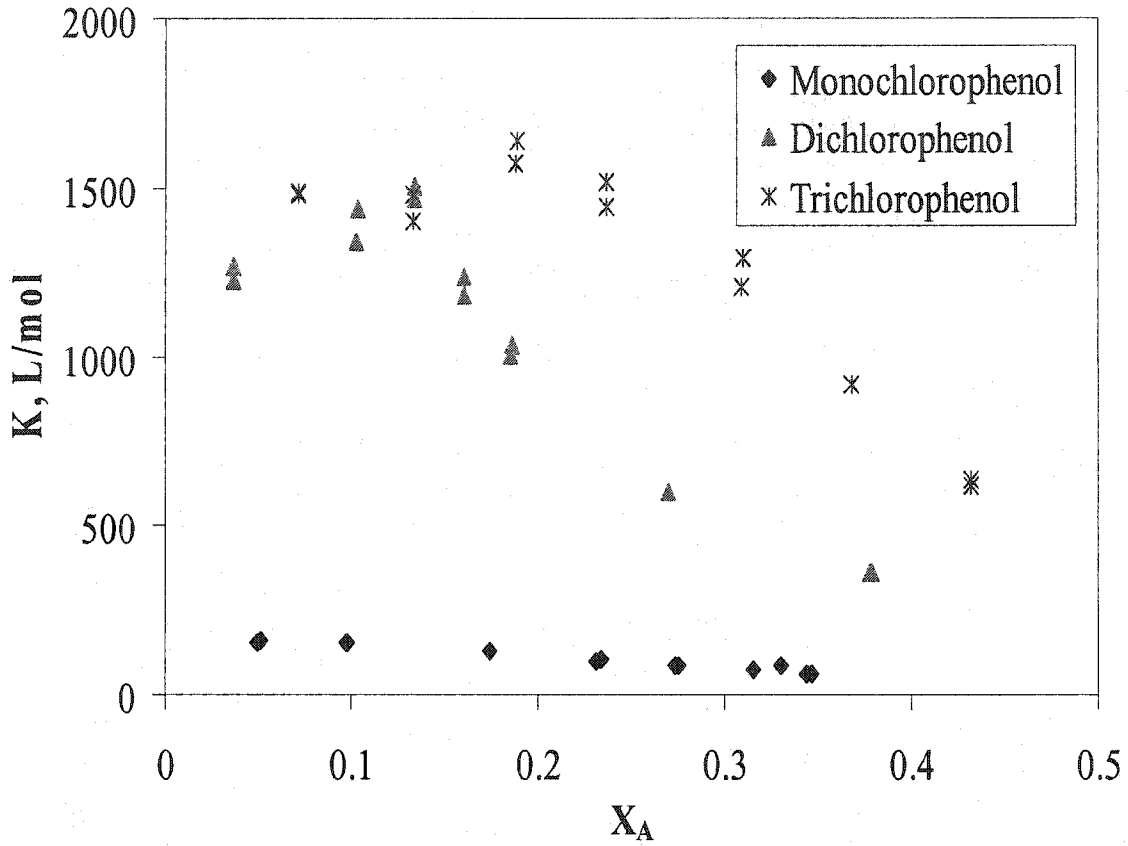


Figure 5. 15 Solubilization equilibrium constant vs mole fraction for different solutes in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 mM. Initial [NaCl] is 0.1 M.

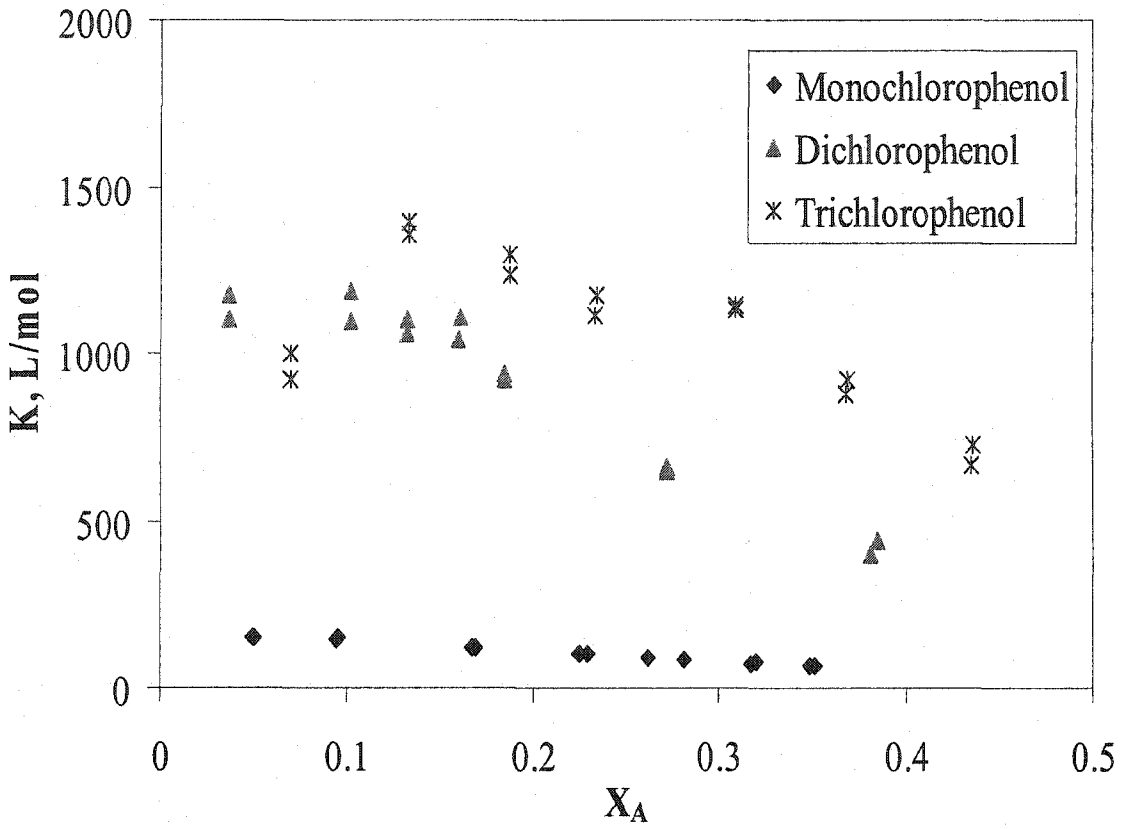


Figure 5. 16 Solubilization equilibrium constant vs mole fraction for different solutes in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively. Initial [NaCl] is 0.05 M.

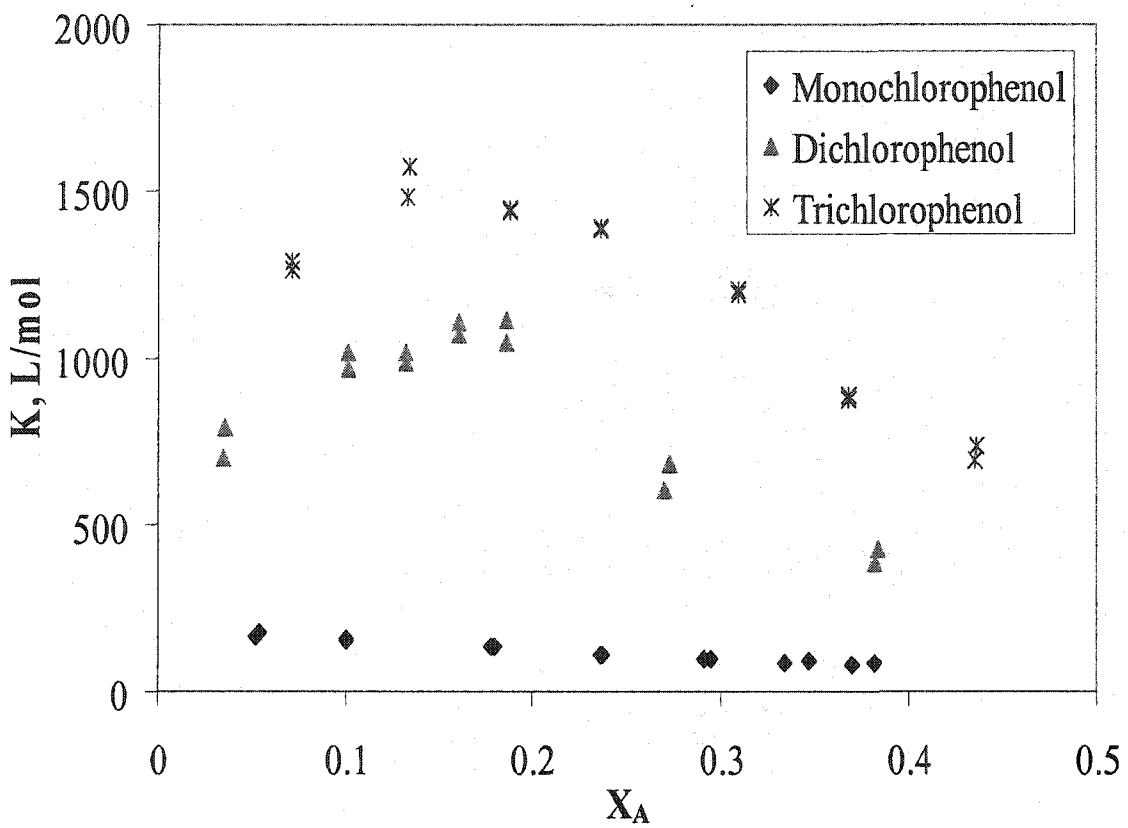


Figure 5. 17 Solubilization equilibrium constant vs mole fraction for different solutes in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 75 mM. Initial [NaCl] is 0.1 M.

CHAPTER 6

COLLOID-ENHANCED ULTRAFILTRATION OF CHLOROPHENOLS IN WASTEWATER: PART 3. EFFECT OF ADDED SALT ON THE SURFACTANT LEAKAGE IN SURFACTANT SOLUTIONS AND SURFACTANT-POLYMER MIXTURES

6.1 Abstract

The critical aggregation concentration (cac) in surfactant - polymer mixtures approximates the surfactant concentration in the permeate in polyelectrolyte micellar-enhanced ultrafiltration or "surfactant leakage" since it approximates the unaggregated surfactant concentration in equilibrium with surfactant - polymer complexes. Here, the cac was measured at different salinities by using surface tension measurements. It was found that the cac increases slightly with the addition of simple salt, then the cac value decreases at higher salt concentration. The surfactant leakage in colloid-enhanced ultrafiltration (CEUF) processes is investigated by using the semiequilibrium dialysis (SED) method in the presence of three phenolic solutes with various degrees of chlorination: 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). Cetylpyridinuim chloride (CPC) or *n*-hexadecylpyridinium chloride is used as a cationic surfactant; and sodium poly(styrenesulfonate) (PSS) is used as an anionic polyelectrolyte. The effect of

salinity, type of colloid, and type of solute is focused evaluated here. It was observed that the added salt reduces the surfactant leakage in the micellar solution due to CMC reduction in the presence of electrolyte. In the surfactant - polymer mixtures, the added salt enhances the surfactant leakage due to an increase in critical aggregation concentration (cac) with increasing electrolyte concentration. In the presence of salt, the surfactant leakage in the micellar solution is less than that in the surfactant - polymer mixtures. Polyelectrolyte concentration is found to influence the surfactant leakage. Maximum surfactant leakage is seen in the system studied with MCP as compared to DCP and TCP in both the micellar solution and the surfactant - polymer mixtures. An important conclusion is that addition of oppositely charged polyelectrolyte to a cationic surfactant can greatly reduce surfactant leakage in the absence of added salt, but at high ionic strength, reduction of surfactant leakage is much less in the presence of the polyelectrolyte.

6.2 Introduction

The properties of surfactants in solutions are governed by their tendency to minimize the contact of their hydrophobic groups with water. This is accomplished by adsorbing at interfaces and association in solution[188]. A plot of Surface tension versus log concentration of surfactants generally exhibits a significant decrease with concentration initially, followed by a sharp break above which the surface tension remains almost constant. The break is due to the formation of surfactant clusters or

micelles and the breakpoint is called the critical micelle concentration or CMC. Above this concentration, almost all of the added surfactant molecules are used to form additional micelles and the monomer concentration does not appreciably increase. Since only the surfactant monomers adsorb at the interface, the surface tension remains essentially constant above the CMC. Therefore, the surface tension can be directly related to the activity of monomers in the solution.

Surfactants and polymers are often used together in industrial applications. When present together, they can interact to provide beneficial properties. Owing to their industrial importance, aqueous surfactant - polymer mixtures are of much interest from both fundamental and technological viewpoints. Surfactant binding to polymers in aqueous solution has been investigated extensively[68-69,74-88]. The interaction often observed between polymers and surfactants in aqueous solution results from one or both of two main driving forces[76,88,189,190]). The first is an electrostatic attraction, generally accepted as an ion-exchange process, where the electrostatic forces of interaction are reinforced by aggregation of alkyl chains of the bound surfactant molecules[190]. The second is a force involving an interaction between hydrophobic groups on the polymer and those of surfactant molecules in their incipient aggregation process[88,189]. It was found that when dodecyltrimethylammonium ions ($C_{12}TA^+$) aggregate in solutions of hydrophobic polyelectrolyte, hydrophobic parts of the polyelectrolyte are taking part in the micellar structure[191]. On the other hand, with a hydrophilic polyelectrolyte, the interaction with surfactant is expected to be mainly electrostatic[87].

Micelle-like organized structures can occur even at concentrations several orders of magnitude lower than the CMC of the surfactant[79,174-176]. The concentration at which the micelle-like organized structure occurs is called critical aggregation concentration or cac. The overall picture for interaction within oppositely charged surfactant - polymer systems is described as follows: at low surfactant concentration, the ionic surfactant head groups individually bind to the oppositely charged polymer due to electrostatic attraction. When the surfactant concentration exceeds the cac, the polymer-bound surfactant aggregate forms, resulting in the formation of surfactant - polymer complexes[190]. Increasing surfactant concentration leads to an increase in surfactant - polymer binding, until the polymer becomes saturated with the surfactant[173]. The surfactant - polymer complex has been described as "micelles on a string" or "beads on necklace" in which the polymer chain connects micelle-like surfactant aggregates by wrapping around them[69,77,82].

Surface tension measurements afford a simple and informative method of studying mixtures of two components, one of which is highly active and the other is relatively inactive at the air - water interface. The surface tension results are used to investigate the surfactant - polymer interaction as well as to determine the cac[42,76, 84,86,122,125,192-195]. A schematic representation of the surface tension curve with generally accepted aggregate structures in each surfactant concentration regime is shown in Fig. 3.9[42,189,193]. The general features of the surface tension trends are as follows: (i) a synergistic lowering of surface tension at very low surfactant concentration regime or region a-b-c is observed, implying the formation of a highly

surface-active complex and also indicating the beginning of cooperative adsorption of the polymer and the surfactant[193], (ii) the surface tension reaches a plateau at region c-d where the addition of the surfactant above point c contributes to the formation of the surfactant - polymer complexes, (iii) eventually, coincidence with the surface tension curve of the polymer-free surfactant system in the micellar region, after point e[189]. It is commonly known that the cac can be deduced from the surface tension versus surfactant concentration plot as shown in Fig. 3.9, as point c[125122].

Several investigators have studied the effect of salt in dilute systems of polyelectrolyte and oppositely charged surfactant[69,71,84,86,93,96-97]. It was found that the cac increases when simple salt is added. This suggests that the interaction between polyelectrolyte and surfactant is reduced by the addition of salt. A study of the effect of simple salt on the surfactant binding by Kogej and Škerjanc shows that any increase in the ionic strength of solution shifts the onset of binding toward higher free surfactant concentrations and decreases the amount of bound surfactant[68]. Hayakawa and Kwak observed that a higher added salt valency results in a larger increase in the cac[71]. Mattai and Kwak found that the binding of inorganic counterions on the polyions shows anticooperatively, presumably due to the reduction of electrostatic force as the binding takes place[97]. The effect of added salt is thus opposite to the influence of salt in micellar system, where stabilization occurs, manifested by a lowering of the CMC[98-99].

As mentioned previously, the binding of surfactant ions on polyions takes place not only by coulombic attractive force but also by hydrophobic interaction

between bound surfactant ions. Wang and Tam have recently studied the interaction mechanism within oppositely charged surfactant - polymer systems by using isothermal titration calorimetry (ICT)[80]. They found that in the presence of salt, the binding isotherm has three stages corresponding to the electrostatic binding, the micellization of bound surfactant molecules, and the formation of free surfactant micelles. In the presence of excess salt, the binding isotherm follows a similar trend to the curve in a polymer-free system, representing the formation of free micelles. This is due to the fact that the coulombic attractive force between polymer and surfactant is considerably screened, the electrostatic binding is significantly weakened; and consequently the polymer-induced micellization cannot occur since negligible amounts of surfactant are electrostatically bound to the polymer backbone. On the other hand, the coulombic repulsion between the surfactant head groups is also shielded by the addition of salt, which favors the formation of free micelles.

In a previous work[196], we used semiequilibrium dialysis (SED) to demonstrate the effect of added salt on the solubilization in colloid-enhanced ultrafiltration (CEUF) processes. This paper contains additional work on CEUF, which shows the effect of added salt on surfactant leakage in surfactant solutions and surfactant - polymer mixtures. Results of surface tensiometric investigation on the critical aggregation concentration at different salt concentrations are also examined. The effect of solutes structure with different degrees of chlorination is also investigated in this paper.

6.3 Experimental

As seen in our previous work[42], the surfactant leakage can be determined by using the semiequilibrium dialysis technique. A detailed description of the materials and methods for determining the surfactant leakage used here is given in previous papers[42,196]. The surfactant and polyelectrolyte used in this work were cetylpyridinium chloride or CPC and sodium poly(styrenesulfonate) or PSS, respectively. The PSS has an average molecular weight of approximately 70,000 Daltons; the repeating unit of the polymer is $CH_2CH(C_6H_4)SO_3Na$. Organic solutes with various degree of chlorination studied here are monochlorophenol (MCP), dichlorophenol (DCP), and trichlorophenol (TCP).

Surface tension measurements, by means of the Wilhelmy plate technique using Krüss Processor Tensiometer K12 (Krüss USA, North Corolina), were performed on solutions (at pH 3). The detailed method was previously decribed in section 3.3.2. Repeated surface tension measurements were made until readings were within 0.02 mN/m. The equilibrium time was found to depend on the type of solution, and all measurements were made at equilibrium.

6.4 Results and Discussion

6.4.1 Surface Tension

The surface tension of 50 mM PSS solutions in the presence and absence of salt was measured as a function of CPC concentration in the absence of solute, as shown in Fig. 6.1, where a synergistic lowering of surface tension at low CPC concentration due to the PSS is observed. As found in a previous study[42], the PSS can have a massive effect on surface tension lowering; therefore, a dramatic reduction in surface tension is observed even at 0.002 mM CPC. According to Fig. 3.9, this results in the absence of region a-b, or point b is buried in region a-b-c. The cac is determined by the intersection between 2 straight lines drawn on region a-b-c and c-d. An apparent step is observed before the surface tension reaches the plateau region. Previous work found that this plateau surface tension is mildly dependent on PSS concentration but it is attained at a lower CPC concentration as PSS concentration increases[42]. At higher surfactant concentration in the plateau region, the surface tension slightly increases as the surfactant concentration increases. The surface tension decreases as the surfactant - polymer concentration ratio becomes close to 1 to 2. The surface tension continues to decrease to which the precipitation is observed at the surfactant to polymer ratio of 1 to 1. It should be noted that the repeating unit of the PSS is $CH_2CH(C_6H_4)SO_3Na$ and the CPC structure is $C_{21}H_{38}NCl$. As the surfactant and polymer stoichiometrically associate, the precipitation can be expected.

Kogej and his coworkers also observed phase separation when the [CPC] to [PSS] concentration ratio becomes unity[197]. As shown in Fig. 6.1, the cac corresponding to the point where the surface tension reaches the plateau region is approximately equal to a CPC concentration of 0.006 mM in the absence of salt. In the presence of 0.05 M NaCl, the cac increases to 0.0075 mM CPC. However, at higher salt concentration, the cac is observed to decrease; the cac in the presence of 0.1 M and 0.2 M NaCl is approximately 0.005 mM CPC. It should be noted that the lines drawn for the systems in the presence of 0.1 M and 0.2 M NaCl coincide, giving the same cac value.

The surface tension behavior is different from that normally observed for surfactant solutions without polymer. For surfactant solutions, a single sharp break in variation of surface tension with surfactant concentration occurs at the CMC. For surfactant - polymer mixtures, the classical pattern of surface tension variation corresponds to two abrupt changes in surface tension at the cac and the CMC[42,125,189-190, 193-195], as also mentioned in Chapter 3. The increase in the surface tension in the plateau region as CPC concentration increases may be due to a certain conformational change as the binding occurring in the region c-d as also observed by Park and coworkers[86]; they proposed that more surfactant can bind to such surfactant - polymer aggregates, resulting in a decrease in free surfactant concentration in the bulk solution interface, and therefore increasing the surfactant tension.

At CPC concentrations above point d, the monomeric CPC concentration increases as the polymer becomes saturated with the surfactant aggregates (refer to Fig. 3.9). At yet higher CPC concentration, eventually ordinary micelles form (point

e) and the surface tension tends to plateau again above the CMC of the surfactant as also observed in previous work[42,125,189-190, 193-195]. It should be noted that point e is the maximum obtainable CPC concentration before phase separation is observed. Our previous work showed that the higher the PSS concentration, the higher the CPC concentration at point e. In other words, if the phase separation does not occur, the CMC tends to occur at higher CPC concentration as the PSS concentration increases[42]. The CPC concentration required to form micelles in the presence of PSS is higher than the CMC because a vast majority of surfactant is present in surfactant - polymer complexes instead of monomer when this micelle formation concentration is attained, compared to the polymer-free surfactant system. However, this CPC concentration was not reached for any of PSS concentration studied previously[42], primarily because the polymer and surfactant form a precipitate prior to this concentration. Hansson and Almgren[87] explained the particular precipitation in that the binding of surfactant to the polyelectrolyte makes the complex more hydrophobic. When their net charge becomes sufficiently low, the complexes will start to attract each other, and, due to hydrophobic nature of the interaction, the water content will be low in the concentrated phase; i.e., a precipitate will be formed. The drastic decrease in surface tension of PSS solutions when the concentration of surfactant exceeds about 50 % of that of PSS is of particular interest. A previous study has measured the surface tension at different PSS concentrations and it was also found that point d corresponds approximately to a CPC - PSS molar ratio of 1/2; this implies that two anionic sulfonate PSS groups stabilize one aggregated cationic surfactant molecule[42].

Therefore, the addition of surfactant exceeding the binding capacity of PSS would increase the concentration of free surfactants, and thus decrease surface tension.

As mentioned earlier, the coulombic interaction between surfactant and polymer is screened by the presence of salt. Therefore, the polymer-bound micellization does not occur as favorably, resulting in an increase in the cac. However at higher salt concentration such as at 0.2 M NaCl, the added salt tends to stabilize the polymer-bound micelle, resulting in a decrease in the cac. This corresponds to a mechanism proposed by Lindman and Thalberg that the effect of salt is twofold[89]: (i) reduction of the electrostatic interaction between polymer and surfactant, and (ii) stabilization of the surfactant aggregates. They projected that the first mechanism will dominate at low ionic strength while the second mechanism will play a more important role at higher ionic strength. Similar to the CMC behavior, the decrease in the cac at high salt concentration can be expected as seen in the present work.

The addition of salt does not change the cac dramatically, probably due to the strong hydrophobic interaction between CPC and PSS. It was found that for systems with a higher degree of binding, the free and bound surfactant is approximately constant with the addition of salt whereas the concentration of free surfactant increases with increasing salt concentration for systems with a lower degree of binding[74]. For systems where the polyelectrolyte contains hydrophobic moieties (such as PSS), the interaction with surfactant is stronger, and the effect of salt on the cac is smaller[69] than for hydrophilic polyelectrolytes (e.g. sodium polyacrylate or PA). This indicates that

there is a hydrophobic interaction not only between the surfactants but also between the surfactant and polymer. We emphasize that the purpose of the cac determination is not to correctly estimate the surfactant monomer concentration but to illustrate how the salt affects the surface activity, and therefore the surfactant monomer concentration or the surfactant leakage.

6.4.2 Surfactant Leakage

Most surfactant leakage measurements were done without pH adjustment unless it is mentioned otherwise; though the pH of the initial and final solutions was recorded. The reason that pH was not adjusted for higher pH conditions is that the addition of sodium hydroxide (NaOH) causes surfactant degradation. The pH value of the initial and final retentate solutions is shown previously in Table 4.2 and Table 4.3, respectively. The percentage of the phenolate is shown in Table 4. The percentage of the phenolate anion is obtained from the species distribution shown in a previous work[181]. The species distribution was obtained at 0.3 mM solute concentration which is the highest concentration achievable in spectrophotometer measurement that does not violate Beer's law. Therefore, the lowest solute concentration in a series of the SED experiment is selected as a model in order to determine the percentage of the phenolate anion; and this percentage is used to explain the observed behavior.

The experiments at pH 3 were carried out for the system with TCP to control the solute charge. In such experiments, the pH of initial permeate and retentate

solutions was adjusted to 3 where the neutral species of the solutes are predominantly present except the micellar system in the absence of salt, where 11% of the phenolate anion is observed, as shown in Table 4.4. However, the solutions without pH adjustment contain greater percentage negatively charged solute. Without pH adjustment, the surfactant concentration in the permeate or surfactant leakage is plotted as a function of MCP, DCP, and TCP concentration in the retentate in the micellar solutions as shown in Figs. 6.2 through 6.4 and in the surfactant - polymer mixtures as shown in Figs. 6.5 through 6.7 . The pH range of final retentate solutions is showed in parentheses of the figures. The experiments at pH 3 were carried out for TCP in both micellar solutions and surfactant - polymer mixtures as shown by Figs. 6.8 and 6.9, respectively. As shown in Figs. 6.2 through 6.4, the surfactant leakage in the micellar solution is reduced by more than an order of magnitude in the presence of the added salt. When solute concentration increases, the surfactant leakage in the micellar solution in the absence of salt decreases while the surfactant leakage in the presence of salt remains almost constant or slightly increases. However, at pH 3 where only the neutral species are predominantly present except the micellar system in the absence of salt, the surfactant leakage decreases as the solute concentration increases in both the presence and absence of salt, as shown in Fig. 6.8.

It is commonly known that in aqueous solution the presence of electrolytes causes a change in the CMC for ionic surfactants[99]. The effect of electrolyte concentration on the CMC of ionic surfactants is given by Corrin and Harkins[198]; for a

single monovalent counterion, the log of the CMC is a linear function of log of the free concentration of the counterion as follows:

$$\log CMC = -a \log C_i + b \tag{6.1}$$

where a and b are constants for a given ionic head at a particular temperature and C_i is the free counterion concentration. For CPC with added NaCl, chloride anions are the counterion. The depression of the CMC is due mainly to the decrease in thickness of the ionic atmosphere surrounding the ionic head groups in the presence of electrolyte, resulting in a decreased electrical repulsion between the surfactant head groups. Previous work showed that the surfactant leakage in micellar solutions is approximately 20% higher than the CMC values[42]. Therefore, the surfactant leakage is reduced due to the CMC depression in the presence of added salt as seen in Figs. 6.2 through 6.4 and Fig. 6.8. Our previous work found that in the absence of salt, the solute also causes a CMC depression in micellar solutions[42], resulting in the reduction of the surfactant leakage as the solute concentration increases. The solutes studied here are chlorinated phenols, so the reduction in the CMC of the cationic surfactant is due to a reduction in repulsion between the charged surfactant head groups because the solute hydroxyl groups insert themselves into the micellar palisade layer and increase the distance between the head groups. If the solute is ionized to a phenolate anion, the CMC depression due to the presence of solute will be even greater. As seen in Figs. 6.2 through 6.4, the effect of solute concentration is more pronounced in the micellar solutions without salt, as compared to the systems without salt. This is due to a greater percentage of the phenolate anion present in the micellar solution

without salt, primarily for MCP and DCP. For example, 30% of the phenolate anion is observed for MCP in the absence of salt whereas 7% and 4% of the phenolate anion are observed in the micellar solution with 0.05 M and 0.1 M, respectively, as shown in Table 4.4. It can also be viewed that the addition of salt has a significant effect on the CMC reduction; therefore, the effect of the organic solute on the surfactant leakage can be less important.

In the surfactant - polymer systems with 50 mM PSS, as shown in Figs. 6.5 through 6.7, the surfactant leakage increases as the salt concentration increases; however, for the system studied with TCP, the surfactant leakage in the presence of 0.1 NaCl is less than that in the presence of 0.05 NaCl, as shown in Fig. 6.7. In addition, the surfactant leakage increases as solute concentration increases. The same behavior is observed for the systems with 75 mM PSS, so the results are not shown here. As shown in Fig. 6.9, it is seen that the surfactant leakage gradually increases as the salt concentration increases and tends to decrease at high solute concentrations. As the salt concentration further increases to 0.2 M NaCl, the surfactant leakage appears to be less than the surfactant leakage at 0.1 M NaCl. Like the surfactant - polymer system without pH adjustment, the surfactant leakage generally increases as the solute concentration increases, although some data points at high concentration do not follow the trend. It should be noted that the neutral species are predominantly present in the surfactant - polymer mixtures for all systems studied as shown in Table 4.4.

The effect of the added salt concentration on the surfactant monomer concentration can be qualitatively deduced from the cac obtained from the surface

tension measurements, although the cac does not provide the exact surfactant monomer concentration in the bulk solution. As can be seen from the surface tension results in Fig. 6.1, the cac tends to increase with increasing salt concentration up to 0.05 M NaCl; the cac decreases by a salinity of 0.1 M NaCl. The surfactant leakage results correspond to the trend of the cac versus the salt concentration in the surface tension results. The surfactant leakage results at low salt concentration, as shown in Figs. 6.5-6.7, corresponds to the first mechanism hypothesized by Lindman and Thalberg[89], which states that the added salt reduces the electrostatic interaction between polymer and surfactant, resulting in an increase in the cac, and hence surfactant leakage. At higher salt concentration (0.2 M), the second mechanism becomes dominant; the further addition of salt stabilizes the surfactant aggregates, resulting in a decrease in the cac, and therefore surfactant leakage, as shown in Fig. 6.9. However, it is important to note that the cac cannot be correctly interpreted as the concentration of free surfactant at the onset of surfactant - polymer aggregate formation since a fraction of the surfactant molecules would be bound to the polyions when the cac is attained. Thus, one can expect that at the cac, the concentration of free surfactant is lower than the cac. It should also be noted that the surfactant leakage results found in the SED experiment are greater than that found from surface tension results. This can be attributed to the presence of the chlorophenols in the SED experiments because the surface tension experiments were carried out in the absence of the solutes. Part of the reasons is that the chlolophenols may reduce the surfactant -

polymer interaction due to hydrophobic interaction between the solute and the polymer backbone, resulting in the increase in the surfactant leakage.

The data is replotted in Figs. 6.10 through 6.12 to show the effect of type of colloid in the presence of 0.05 M NaCl. It is observed that the surfactant leakage in the micellar system is lower than that in the surfactant - polymer mixture. An increase in the polymer concentration from 50 mM to 75 mM causes an increase in surfactant leakage. In addition, as solute concentration increases, the surfactant leakage increases. The results at 0.1 M NaCl are not presented here due to similarity to the results at 0.05 M NaCl. Figs. 6.13 through 6.15 show the relationship between surfactant leakage and solute concentration in the presence of 0.05 M NaCl to illustrate the effect of solute structure in the micellar solution and the surfactant - polymer mixtures. Maximum surfactant leakage is observed for MCP, compared to DCP and TCP.

A previous study showed that the surfactant leakage is significantly reduced by the presence of polymer[42] because the surfactant - polymer aggregates form at several orders of magnitude below the CMC of the surfactant. However, the surfactant leakage results in Figs. 6.10 through 6.12 show that for high ionic strength water, the use of surfactant - polymer mixtures does not reduce the surfactant leakage in CEUF compared to surfactant-only system. It can be seen that the polymer concentration affects the surfactant leakage; the increases in polymer concentration enhances the surfactant leakage into the permeate. This could be due to an increase in the cac with increasing polymer concentration[87,176].

According to a previous study, the solute structure was found to influence the CMC of the surfactant, and therefore surfactant leakage[42]. It was found that a higher degree of chlorination causes a greater CMC depression due to the solute-micelle interaction. The solubilization results in the previous study suggested that at a given degree of solubilization (X_A), the greater reduction of head group repulsion for the more hydrophobic solutes results in a lower surfactant monomer concentration in the retentate and resulting lower surfactant leakage. Like the polymer-free system, it is reasonable to expect the same qualitative effect of the type of solute on the surfactant - polymer systems. However, the surfactant leakage in the surfactant – polymer system at 50 mM PSS and 0.05 M NaCl is higher than the value observed in the surface tension result as shown by the dash line in Fig. 6.14. This could be due to that the presence of solute effect the surfactant monomer concentration in the SED experiment.

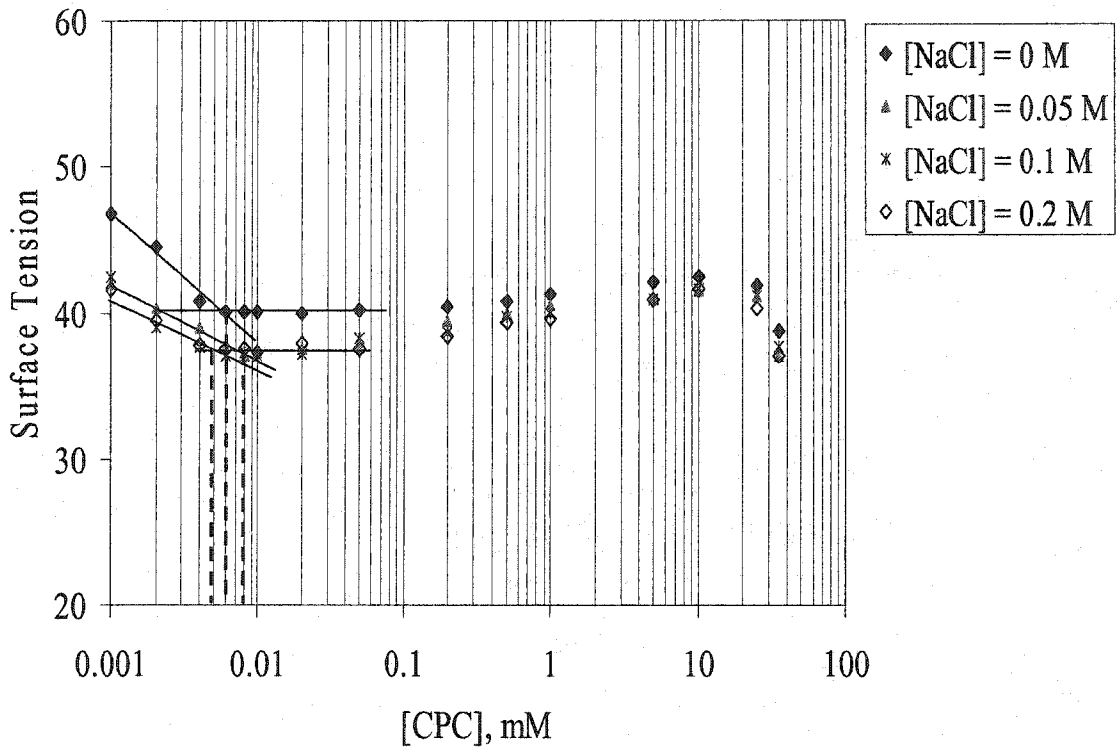


Figure 6. 1 Surface tension of surfactant - polymer system in the absence and presence of salt. [CPC] and [PSS] are 25 and 50 mM, respectively.

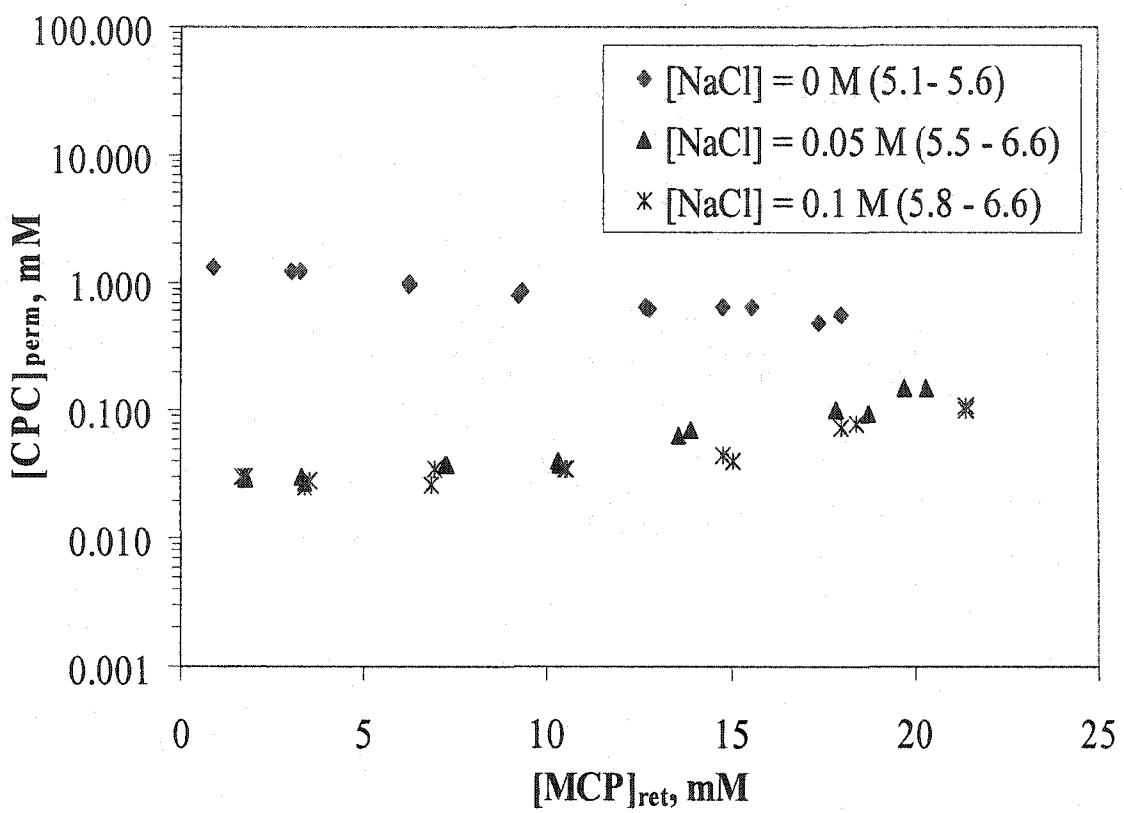


Figure 6. 2 Surfactant leakage in the permeate vs concentration of MCP in the retentate at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

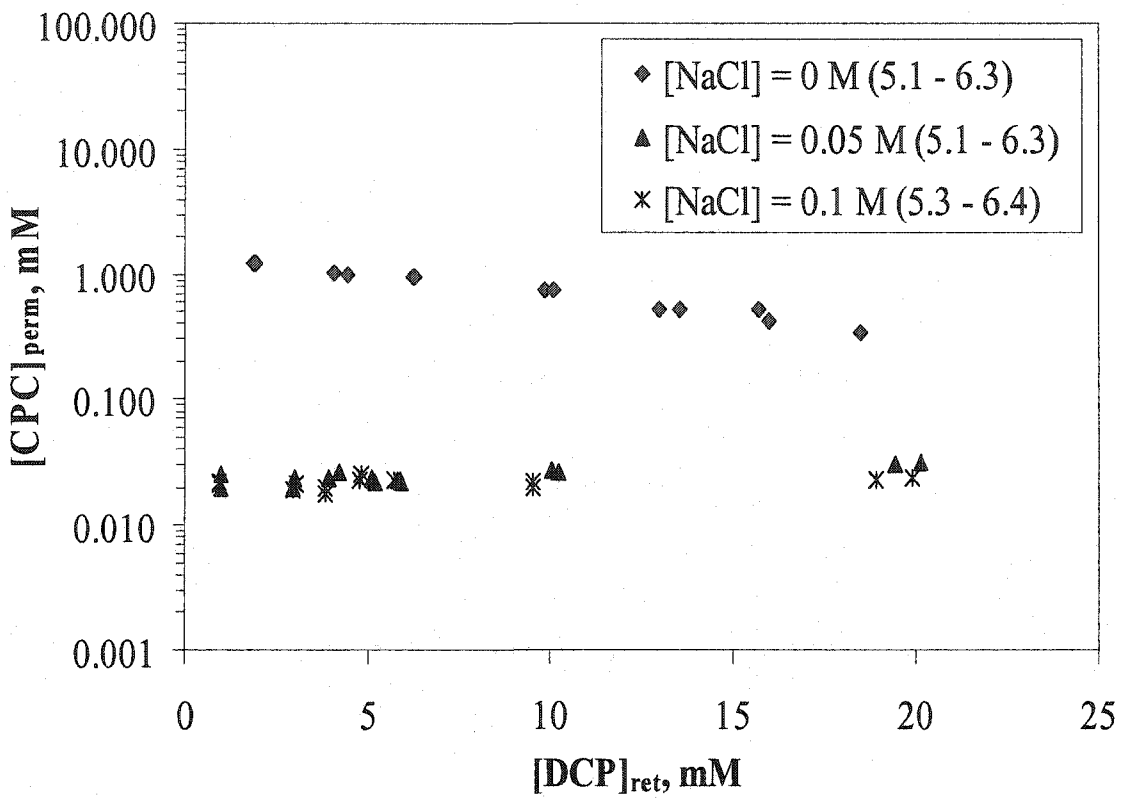


Figure 6. 3 Surfactant leakage in the permeate vs concentration of DCP in the retentate at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

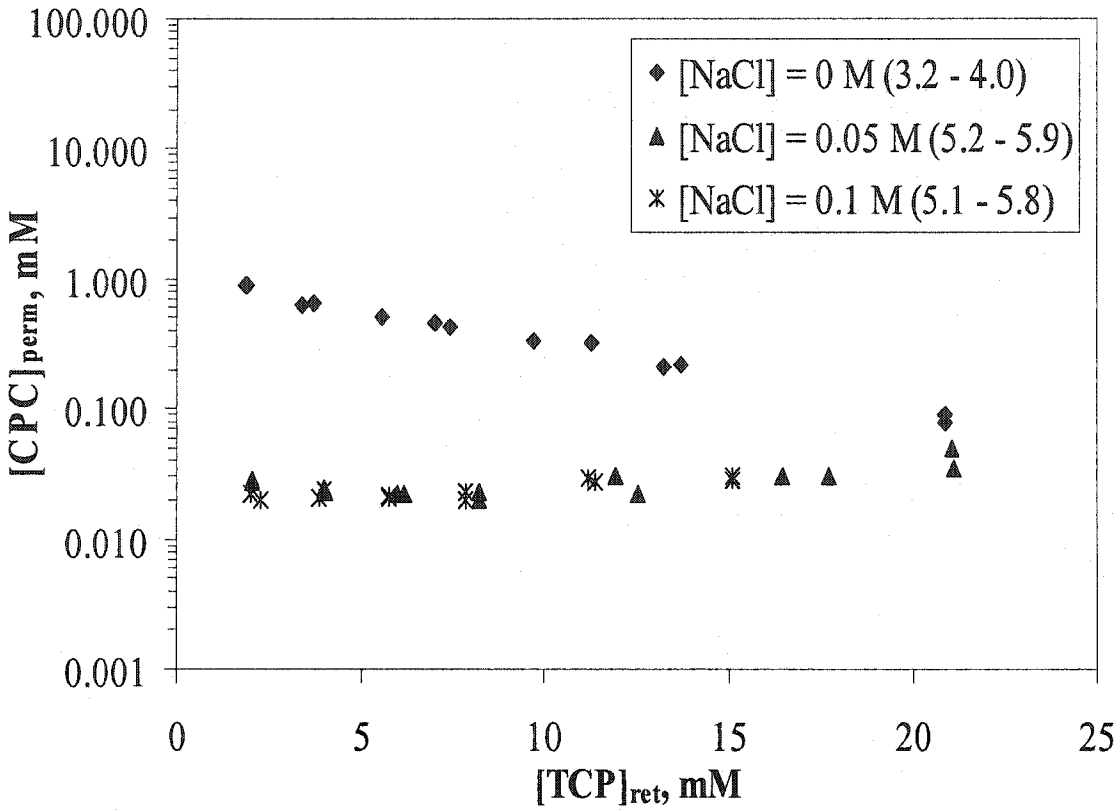


Figure 6. 4 Surfactant leakage in the permeate vs concentration of TCP in the retentate at different NaCl concentrations in CPC micelles. Initial [CPC] is 25 mM.

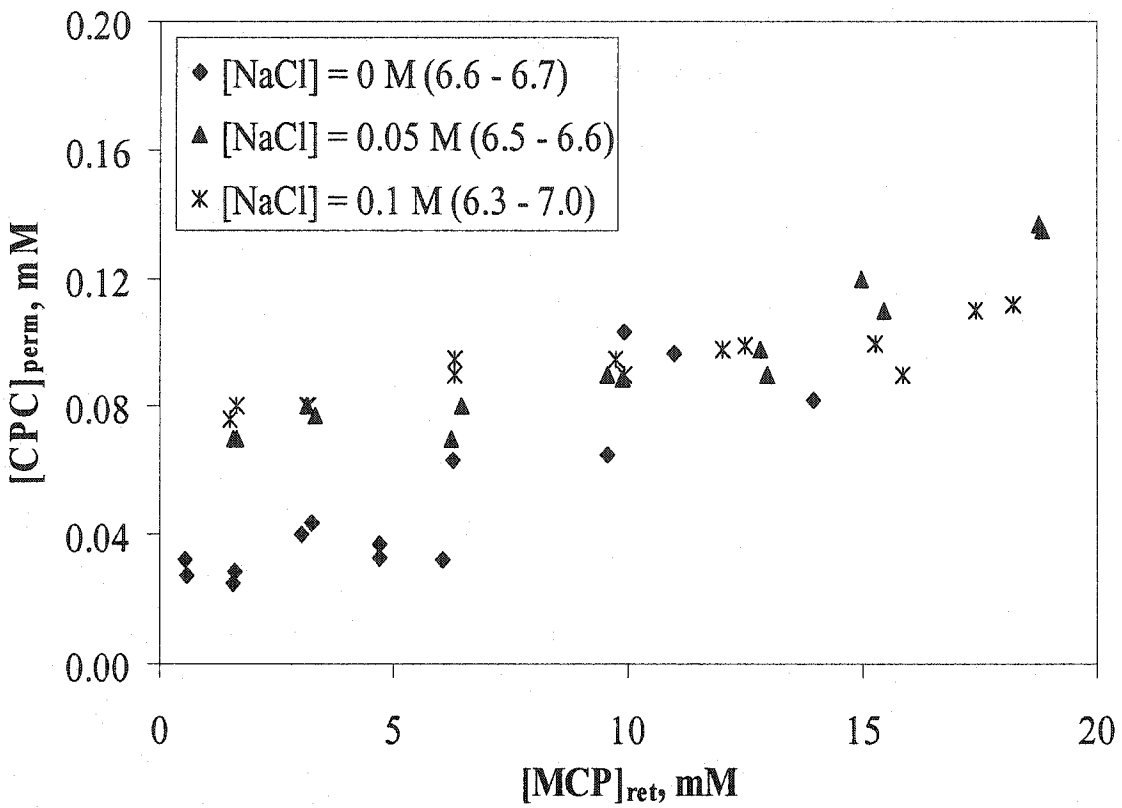


Figure 6. 5 Surfactant leakage in the permeate vs concentration of MCP in the retentate at different NaCl concentrations in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

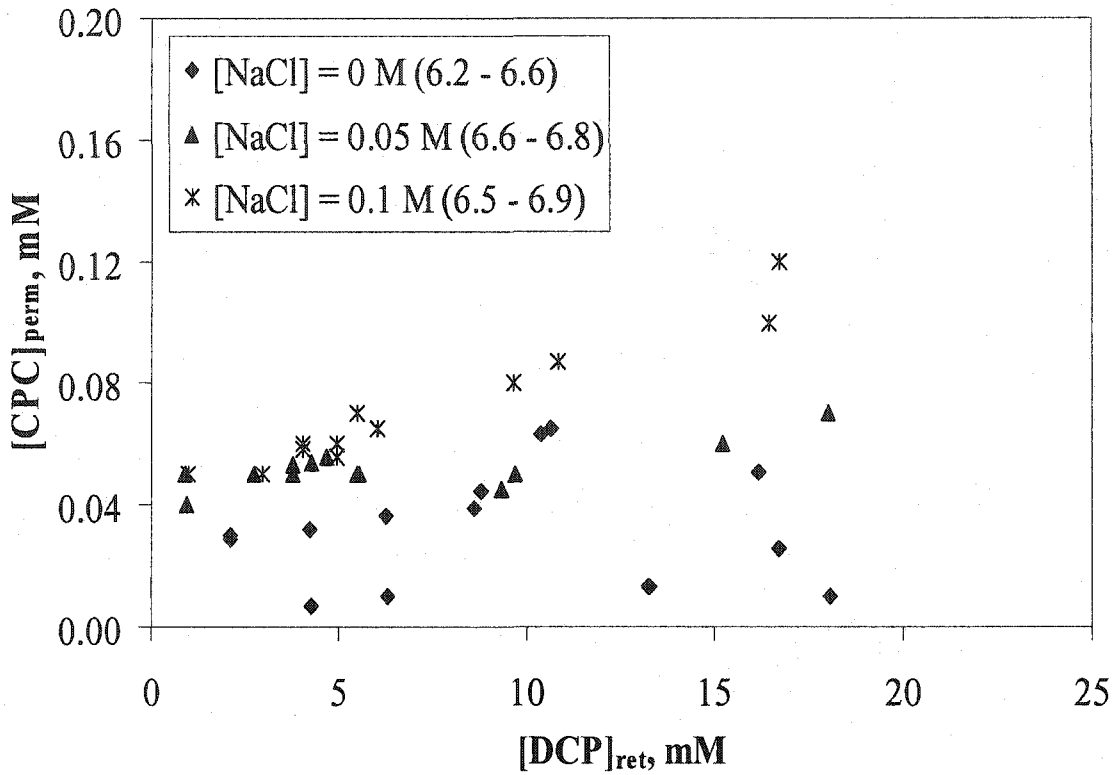


Figure 6. 6 Surfactant leakage in the permeate vs concentration of DCP in the retentate at different NaCl concentrations in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

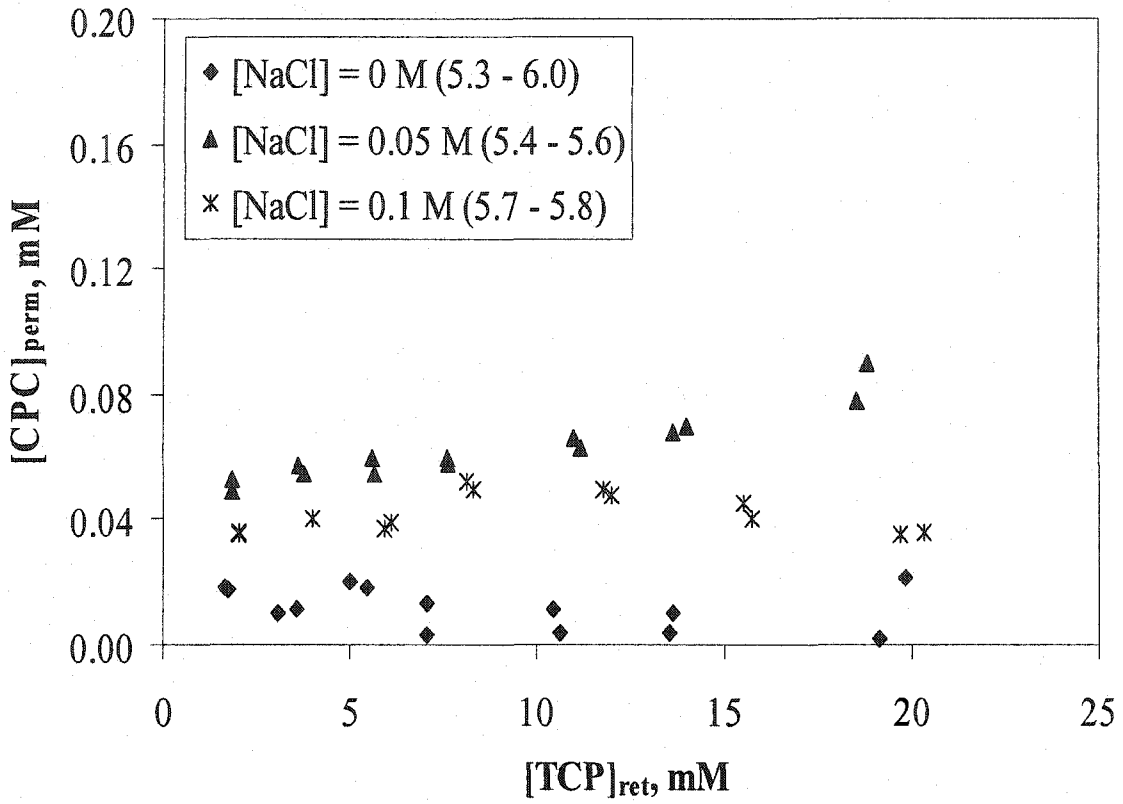


Figure 6. 7 Surfactant leakage in the permeate vs concentration of TCP in the retentate at different NaCl concentrations in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively.

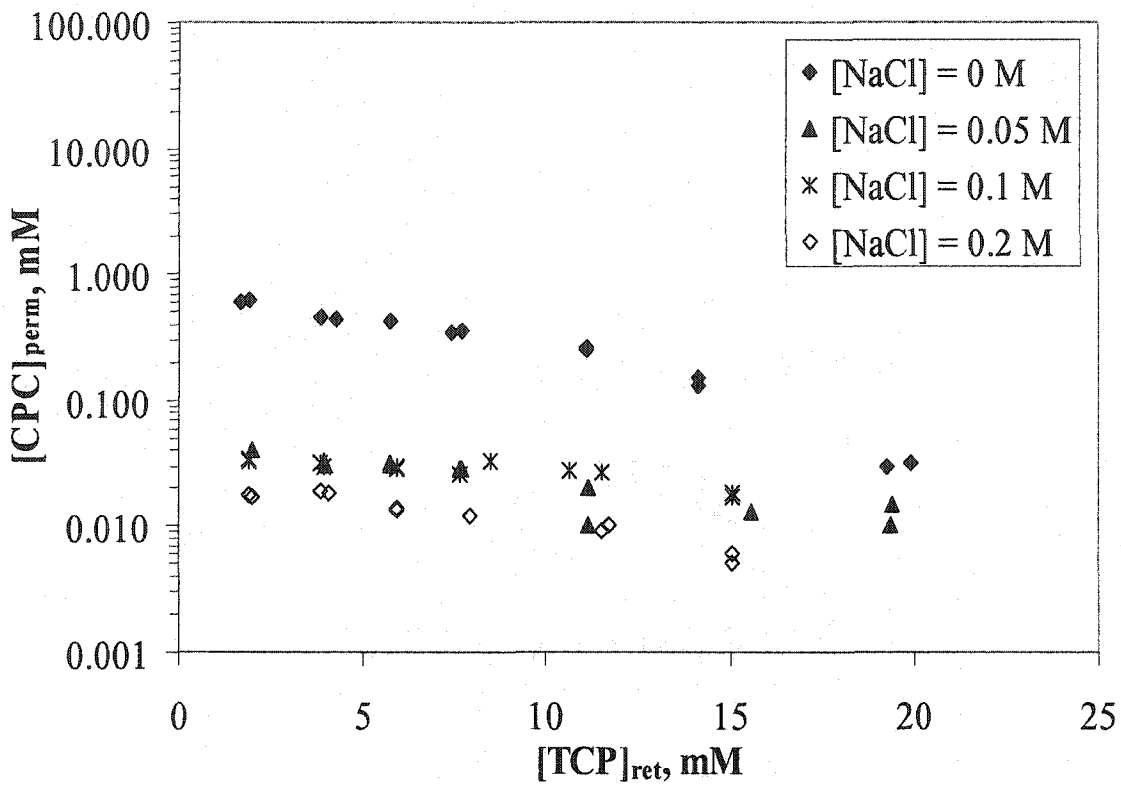


Figure 6. 8 Surfactant leakage in the permeate vs concentration of TCP in the retentate at different NaCl concentrations in CPC micelles at pH of 3. Initial [CPC] is 25 mM.

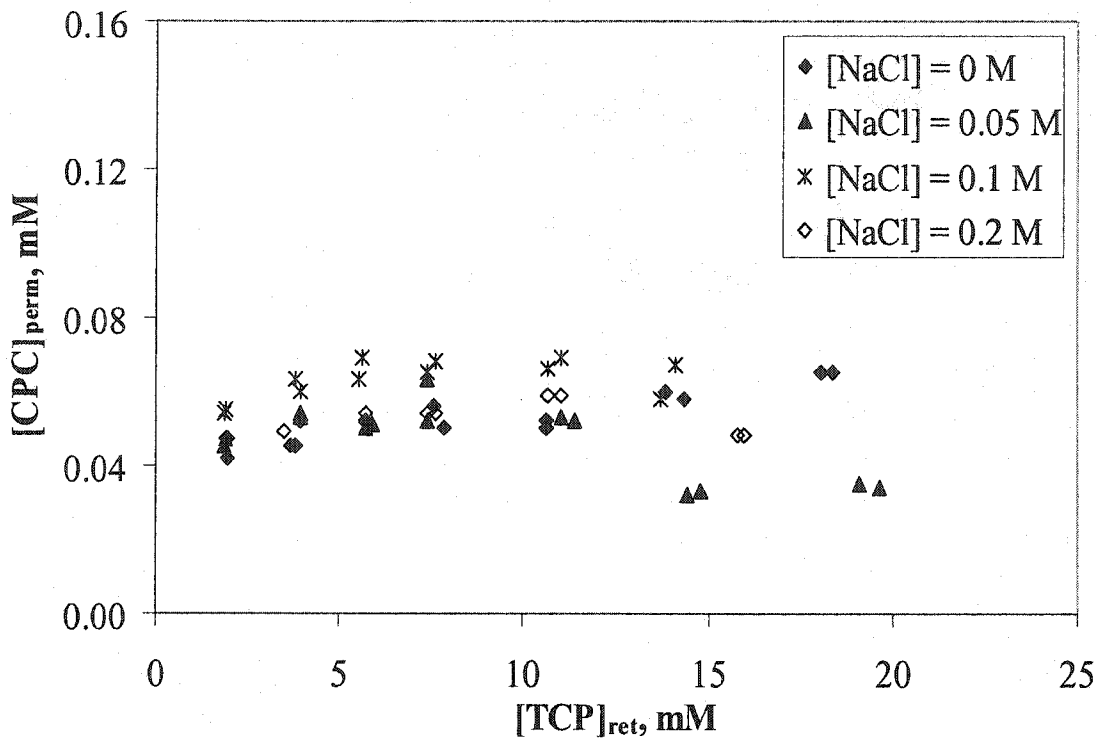


Figure 6. 9 Surfactant leakage in the permeate vs concentration of TCP in the retentate at different NaCl concentrations in CPC - PSS complexes at pH of 3. [CPC] and [PSS] are 25 mM and 50 mM, respectively.

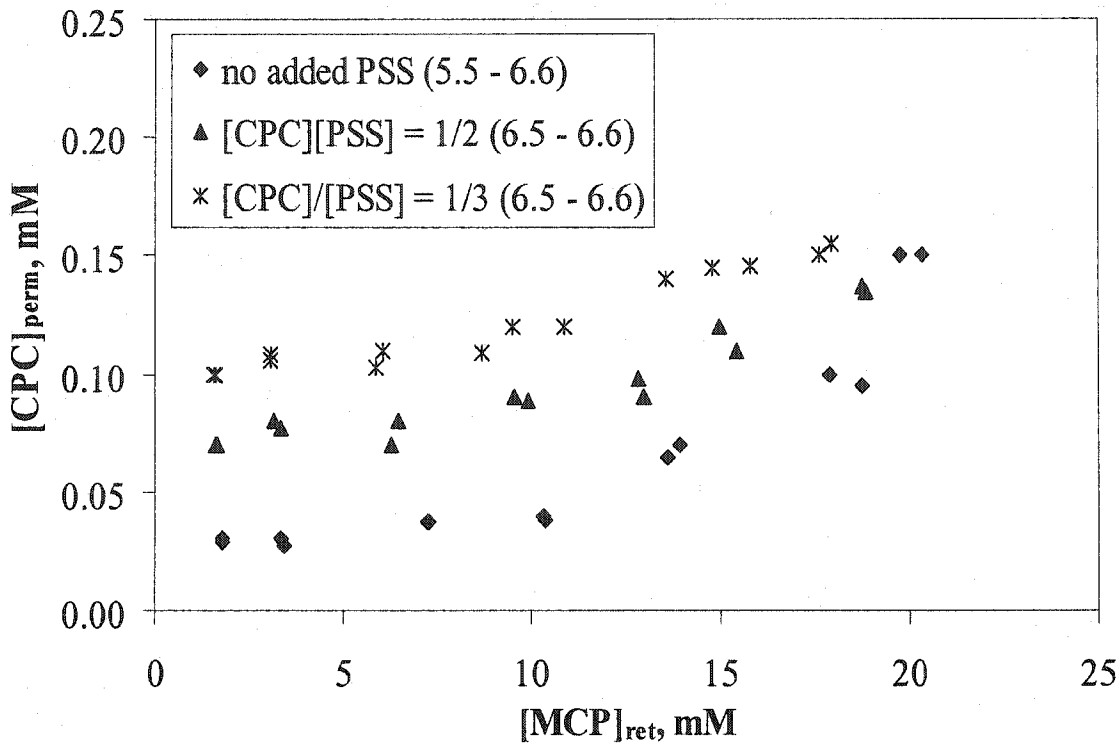


Figure 6. 10 Surfactant leakage in the permeate vs concentration of MCP in the retentate in different types of colloid. Initial [CPC] to [PSS] are 25 mM to 0 mM (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3). Initial [NaCl] is 0.05 mM.

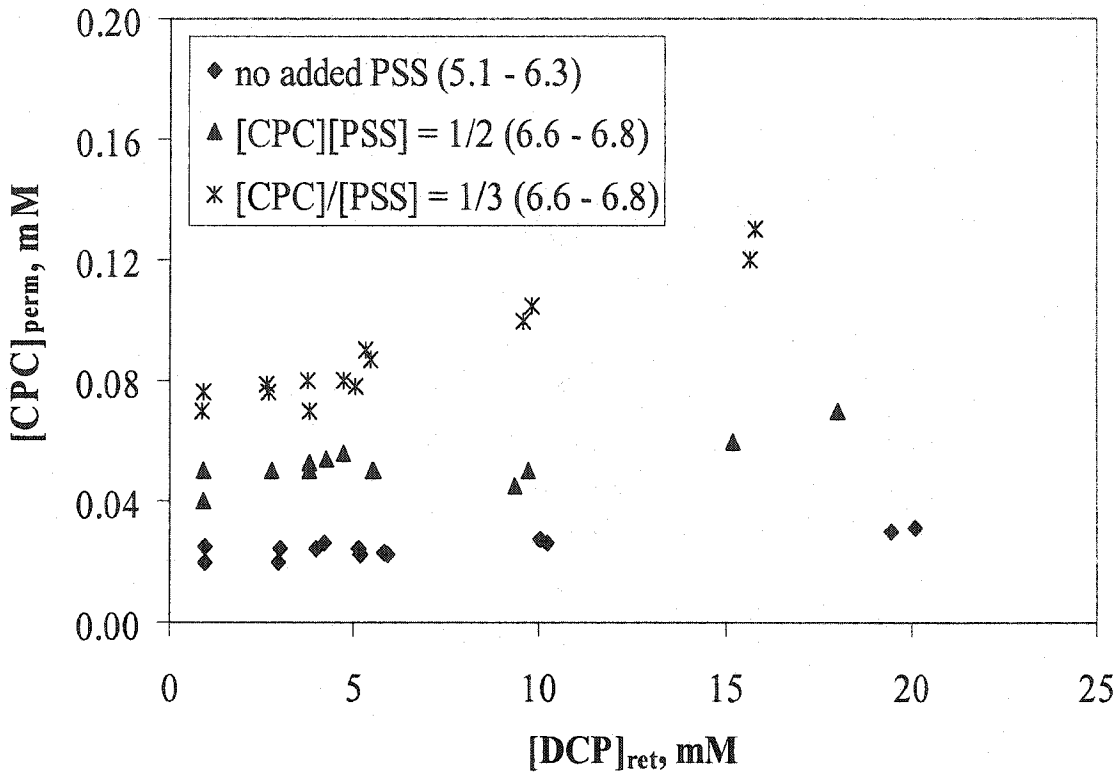


Figure 6. 11 Surfactant leakage in the permeate vs concentration of DCP in the retentate in different types of colloid. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3). Initial [NaCl] is 0.05 mM.

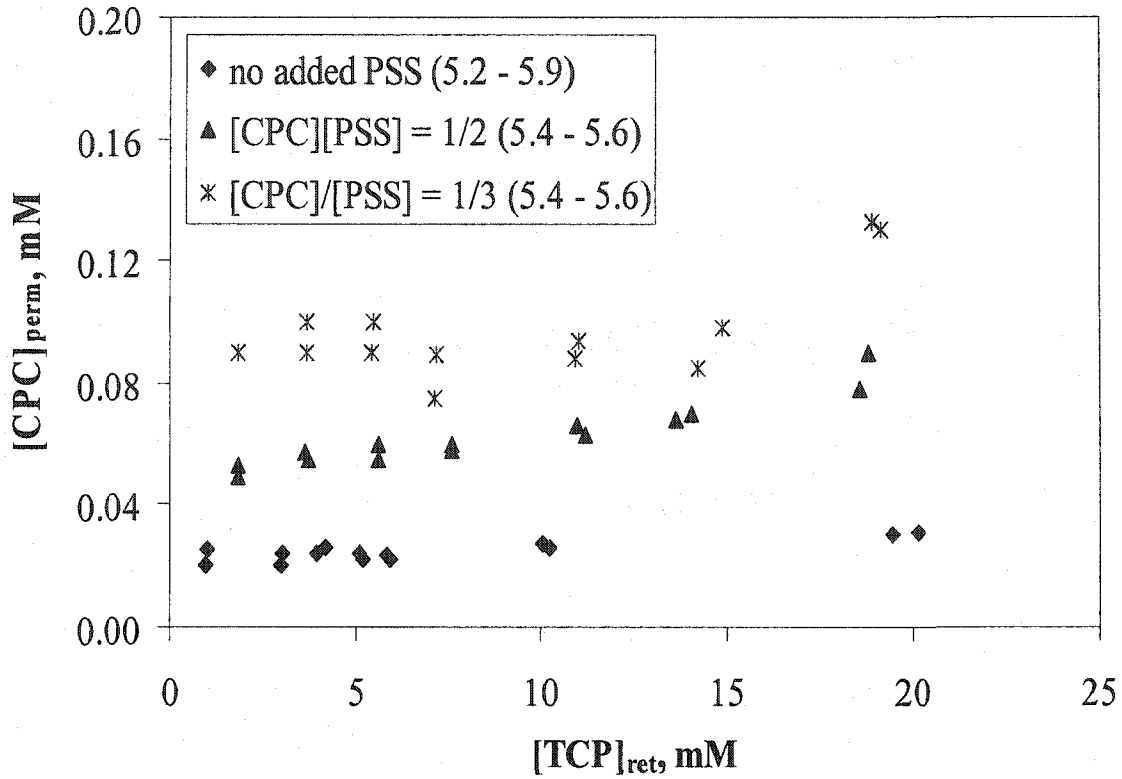


Figure 6. 12 Surfactant leakage in the permeate vs concentration of TCP in the retentate in different types of colloid. Initial [CPC] to [PSS] are 25 mM to 0 (no added PSS), 25 mM to 50 mM (mole ratio 1:2), and 25 mM to 75 mM (mole ratio 1:3). Initial [NaCl] is 0.05 mM.

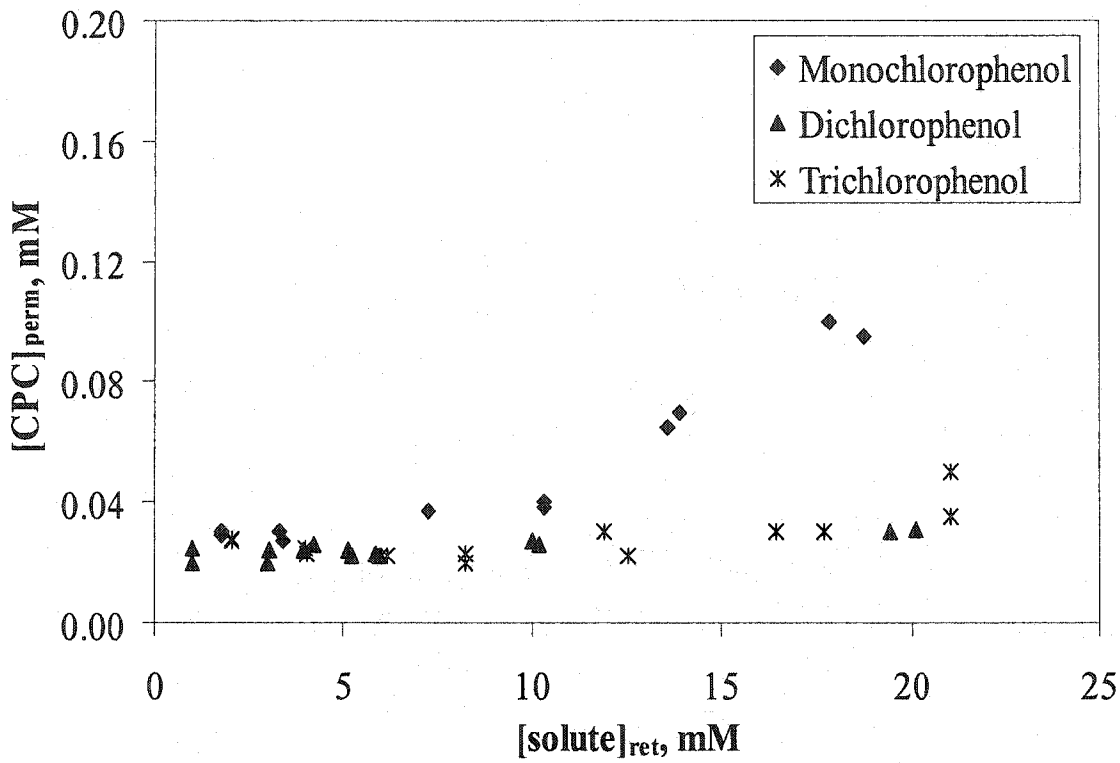
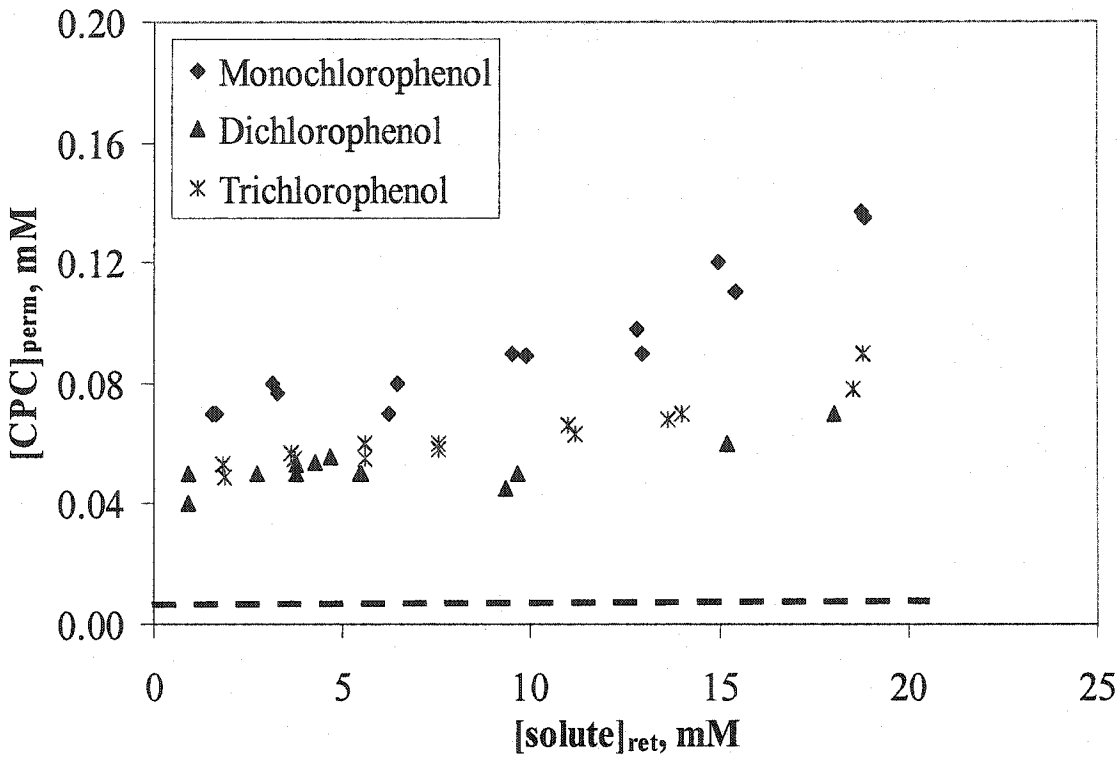


Figure 6. 13 Surfactant leakage in the permeate vs solute concentration in the retentate in CPC micelle. Initial [CPC] is 25 mM. Initial [NaCl] is 0.05 M.



– – – $[CPC]_{monomer}$ in the CPC-PSS mixture (50 mM PSS) at zero solute concentration in the presence of 0.05 M NaCl (from surface tension result)

Figure 6. 14 Surfactant leakage in the permeate vs solute concentration in the retentate in CPC micelle. Initial [CPC] and [PSS] are 25 mM and 50 mM, respectively. Initial [NaCl] is 0.05 M.

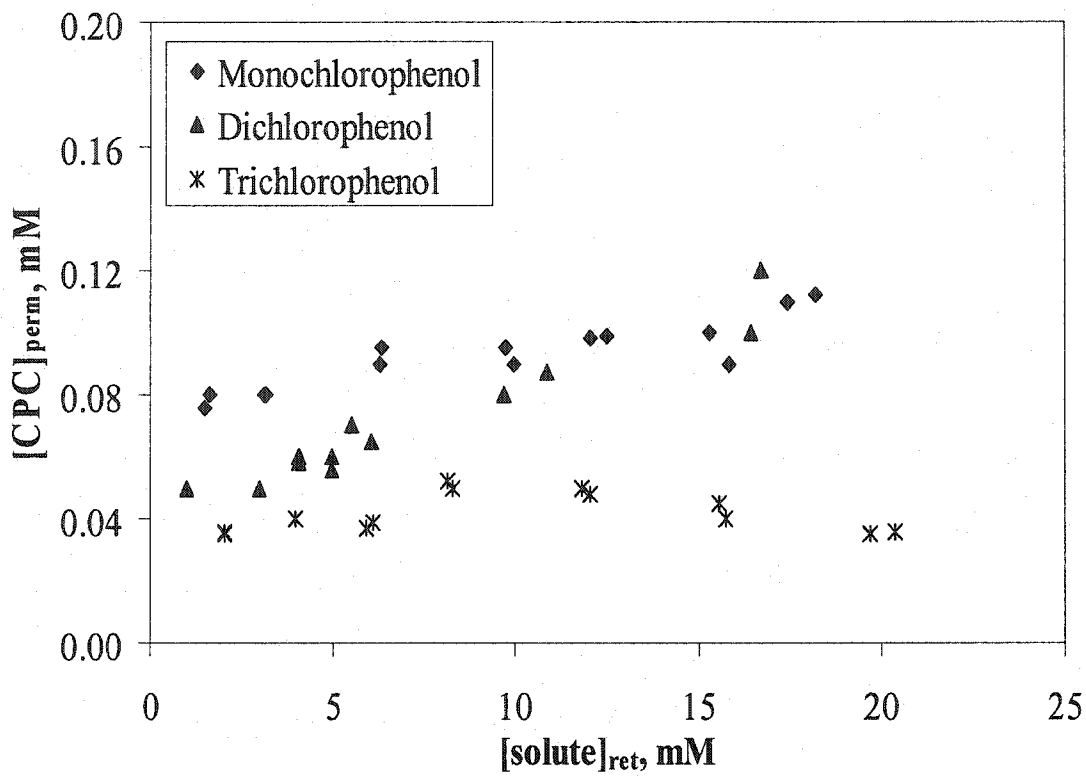


Figure 6. 15 Surfactant leakage in the permeate vs solute concentration in the retentate in CPC - PSS complexes. Initial [CPC] and [PSS] are 25 mM and 75 mM, respectively. Initial [NaCl] is 0.05 M.

CHAPTER 7

COLLOID-ENHANCED ULTRAFILTRATION OF CHLOROPHENOLS IN WASTEWATER: PART 4. SIMULTANEOUS REMOVAL OF A CHLOROPHENOL AND A METAL ION

7.1 Abstract

Polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF) is a separation process to remove target solutes from water using a mixture of a surfactant and an oppositely charged polyelectrolyte as a colloid. An organic solute and a metal cation can simultaneously bind to the colloid, which is subsequently ultrafiltered from solution. An organic solute solubilizes in the surfactant micelle-like aggregates whereas an inorganic cation binds onto the oppositely charged polyion chains. The solution is then passed through the membrane having pore sizes small enough to block the passage of the surfactant - polymer aggregates. In this work, PE-MEUF has been applied to mixtures containing dichlorophenol (DCP) and magnesium (Mg^{2+}), using cetylpyridinium chloride (CPC) and sodium poly(styrenesulfonate) (PSS) mixtures. It was observed that the presence of Mg^{2+} does not affect DCP rejection. In addition, [CPC] to [PSS] ratio and colloid concentration have a significant effect on both DCP and Mg^{2+} rejections. Increased ionic strength from added salt increases the gel point

(colloid concentration at which flux is zero). The viscosity of the colloid solutions is inversely related to the gel point.

7.2 Introduction

Wastewater streams containing dissolved organics are a common problem in the chemical industry. For example, highly toxic and persistent chlorinated phenolic compounds are formed during pulp bleaching when chlorine and chlorine derivatives are used and can be found in wastewater from pulp and paper mills. Non process elements (NPEs) such as Mg^{2+} and Cu^{2+} are also found during pulping. These organic compounds and the NPEs must be removed before the water can be discharged to the environment or reused in the process. However, ordinary ultrafiltration technique is ineffective in the removal of these low molecular weight compounds which simply pass through small pore membranes.

Colloid-enhanced ultrafiltration (CEUF) methods are novel separation processes for removing organic solutes or multivalent ions from aqueous streams. A comprehensive discussion of CEUF processes was cited in a previous paper[42]. Micellar-enhanced ultrafiltration (MEUF) is one technique in which a micellar solution is added to a contaminated feed solution. Polyelectrolyte micellar-enhanced ultrafiltration (PE-MEUF) is a modified MEUF technique where a surfactant-polymer mixture is used as the colloid solution. This solution is then passed through a membrane, which has pores small enough to block the passage of micelles or surfactant-polymer complexes, removing the surfactant aggregates and solubilized

organic solute. The permeate contains very low concentrations of organic solute and surfactant, and it can be discharged or recycled. The retentate contains very high concentrations of both solute and surfactant and has a much lower volume than the original process stream. In previous papers[14-19], we have shown that the concentration of solute in the permeate (solution passing through the membrane) is approximately that expected if the system were at equilibrium; i.e., the permeate concentration is equal to the unsolubilized solute concentration in the retentate. Therefore, equilibrium solubilization measurements such as equilibrium dialysis (ED) or semiequilibrium dialysis (SED) can be used to determine the process efficiency of MEUF and PE-MEUF.

An equilibrium dialysis (ED) method has been used to measure solubilization of solute in surfactant micelles and surfactant – polymer mixtures. For the ED experiment with surfactant-only system, the surfactant concentration in the permeate generally increases to the same concentration as the monomer in the retentate. Then, the permeate surfactant concentration slowly increases as micelles form in the permeate. Since the permeate micelles could solubilize the solute, the permeate solute concentration is greater than the unsolubilized concentration in the retentate. Therefore, either the equilibration time must be chosen to be short enough so that an insignificant concentration of micelles is formed (although long enough to permit the unsolubilized solute to reach equilibrium). This is called "semiequilibrium dialysis or SED" experiment. However, in the polymer-surfactant system, the polymer is almost completely rejected by the membrane, so is present in insignificant concentration in

the permeate[32], therefore no surfactant – polymer aggregate forms in the permeate. Thus, this is called "equilibrium dialysis or ED" experiment.

One of the most important advantages of PE-MEUF is the ability to simultaneously remove dissolved organics and multivalent ions as depicted in Fig. 7.1. The organic solute will solubilize in the micelles whereas the divalent metal cation will bind onto the anionic polyelectrolyte chain. Dunn et al. has demonstrated a simultaneous removal of dissolved organics and multivalent metal cations from wastewater using MEUF[21]. They found that the presence of small concentrations of added multivalent counterions had no significant effect on rejection of the organic solutes. A unique characteristic of PE-MEUF as opposed to MEUF is that the oppositely charged polyelectrolyte stabilizes the surfactant aggregate so the colloid is in equilibrium with a much lower surfactant monomer concentration, which results in the significant reduction in surfactant concentration in the permeate passing through the membrane or surfactant leakage[42,199] at low electrolyte concentration.

In our previous work[42,196,199], we have performed an extensive series of both SED and ED experiments to investigate the solubilization of chlorophenols in micellar solutions and surfactant-polymer mixtures in the presence and absence of salt. It was found that both MEUF and PE-MEUF showed high solubilization constants, primarily for low water solubility solutes such as trichlorophonol (TCP). The added salt enhances the solubilization constant in the surfactant micelles whereas it decreases the solubilization constant in surfactant-polymer complexes[196]. The surfactant leakage in MEUF is reduced by the addition of salt due to critical micelle concentration (CMC)

reduction. However, in PE-MEUF, the surfactant leakage increases as salt concentration increases, primarily due to an increase in the critical aggregation concentration or cac[199].

This paper is a continuation of our previous work on using surfactant-polymer mixtures in the CEUF process. The primary purpose of this paper is to demonstrate the simultaneous removal of a chlorophenol and a divalent metal ion by using surfactant-polymer mixtures, and to measure the gel point for PE-MEUF at different salinities. Viscosity measurements are conducted to help interpret the gel point results.

7.3 Experimental

Dichlorophenol (DCP) and magnesium ion are used as the organic solute and the divalent cation, respectively. The detailed description for all materials used in this study is given in the previous chapters. Magnesium chloride was obtained from Fisher Scientific (Fair Lawn, NJ). A description of equilibrium dialysis or ED experiments was detailed on the previous work[42,196,199]. The ultrafiltration experiments were performed in a 400 mL stirred cell (Amicon 8400, Millipore) at 25 °C and 414 kPa (60 psig) pressure using nitrogen gas. Spectrum 10,000 Da Molecular weight cut-off (MWCO) cellulose acetate membranes were used. A 300 mL solution of Mg^{2+}, DCP, and CPC - PSS mixture at pH 3 (only neutral species are present) was placed in the stirred cell wrapped with plastic tubing through which circulates temperature-controlled water to control the solution temperature to 25 °C. The solution was stirred

at a speed of approximately 800 rpm. The first 10 mL of permeate sample was discarded. Eight permeate samples of 25 mL each were collected, leaving approximately 90 mL of retentate solution. Fluxes were measured during the run by recording the time to accumulate each permeate sample. The concentration of the surfactant and the solute in the permeate was analyzed by using a Hewlett-Packard HP 8452A diode array spectrometer. Magnesium concentration was determined by using a Varian atomic absorption spectrophotometer (AA 30).

The viscosity was measured with a capillary viscometer (Wescan Viscometer Assembly) with optical system attached. The viscometer is connected to a Viscosity Timer (Model 221, Wescan) and immersed in a thermostated bath at 25°C ± 0.1 °C. Flow times could be measured to the nearest 0.01 second. The volume of all samples in the viscometer is kept constant at 30 mL to control the hydrodynamic pressure. The flow time of water (reference) was approximately 400 s. The reduced kinematic viscosity of the sample was determined by using a simplification of Poiseuille's equation as follows:

$$\upsilon_{sample} = \upsilon_{ref}\left(\frac{t_{sample}}{t_{ref}}\right) \tag{7.1}$$

where υ_{sample} is the kinematic viscosity of a sample, υ_{ref} is the kinematic viscosity of a reference (water) which is water, t_{sample} and t_{ref} are the flow times of the sample and the reference, respectively.

7.4 Results and Discussion

7.4.1 Semiequilibrium Dialysis Experiments

The process efficiency is expressed as retentate-based rejection:

$$\text{Solute rejection (\%)} = (1 - \frac{C_{A,perm}}{C_{A,ret}}) * 100 \qquad (7.1)$$

where $C_{A,perm}$ and $C_{A,ret}$ are the concentration of solute A in the permeate and the retentate solution, respectively.

The effect of Mg^{2+} concentration on Mg^{2+} and DCP rejections is as shown in Fig. 7.2, and on surfactant leakage (permeate surfactant concentration) as shown in Fig. 7.3. It is observed that Mg^{2+} rejection decreases as Mg^{2+} concentration increases, whereas the Mg^{2+} concentration does not significantly influence DCP rejection and surfactant leakage; the DCP rejection and surfactant leakage are approximately 95 % and 0.12 mM, respectively. For surfactant-polymer mixtures, the cationic metal binds onto the negatively charged polymer. At a given colloid concentration, polymer adsorption sites for target ion decreases as metal concentration increases, resulting in a lowered metal rejection. The mechanism by which organic solute and multivalent counterion attach to the surfactant – polymer complexes is different: the organic solute solubilizes in the surfactant micelles while the metal cations bind onto the polyanion chains; therefore, the presence of metal should only affect the solubilization of the organic solute if the polymer – stabilized micelles are affected by chemical binding on the polymer. Consequently, at a given surfactant concentration, the DCP rejection

remains almost constant. The increase in metal concentration might be expected to enhance the surfactant leakage because the increased ionic strength from the metal ion present increases critical aggregation concentration (cac). However, the metal concentration used here is so low that it does not significantly affect the ionic strength of the solution, and therefore, the cac and the surfactant leakage.

The effect of [CPC] to [PSS] ratio on Mg^{2+} and DCP rejections is shown in Fig. 7.4. As [CPC] to [PSS] ratio increases from zero to 0.4, the Mg^{2+} rejection is almost constant at above 99% until the ratio is greater than 0.4 where the rejection starts to decrease; DCP rejection drastically increases, then gradually levels off as [CPC] to [PSS] increases as shown in Fig. 7.4. It should be noted that, in the absence of CPC, although a DCP rejection of 62% is unacceptably low, it is higher than what is expected. The effect of [CPC] to [PSS] ratio on surfactant leakage is shown in Fig. 7.5; we observed that the surfactant leakage increases as [CPC] to [PSS] ratio increases.

At a constant polymer concentration, as CPC concentration increases, available sites on the negatively charged polymer decreases due to surfactant-polymer binding. At low [CPC] to [PSS] ratio, the number of negatively charged sites on the polymer is sufficient for the metal cations to bind, resulting in a maximum Mg^{2+} rejection (99+ %). At a higher ratio than 0.4, the Mg^{2+} rejection decreases due to the fact that the surfactant molecules compete for sites on the polymer. The higher surfactant concentration, the less the available sites on the polymer for the metal to bind, resulting in lower metal rejection, as seen in Fig. 7.4. In contrast, as the [CPC] to

[PSS] ratio increases, the DCP rejection increases because the concentration of polymer-bound micelles increases, and therefore increases the solubilization of the organic solute. As the [CPC] to [PSS] ratio increases above 0.4 or 0.5, the increase in the concentration of the polymer-bound micelles is not significant; hence, the DCP rejection does not drastically increase. Rejection of DCP at 62% in the absence of the surfactant is of interest. This might be attributed to the hydrophobic binding between the organic solute and hydrophobic moiety of the polymer.

It was observed that cetylpyridinium cation is almost quantitatively associated with poly(styrenesulfonate) anion over the whole concentration range studied[200]. According to a previous surface tension measurement[42], further added surfactant in a plateau region in a surface tension-surfactant concentration plot gives an increase in concentration of bound surfactant while the concentration of the free surfactant monomer remains almost constant. After the plateau region, the concentration of the free surfactant monomer starts to increase, resulting in a decrease in surface tension. It should be noted that the plateau region in the surface tension plot ranges from 0.006 to 25 mM [CPC]. From the surfactant leakage result, as shown in Fig. 7.5, the surfactant leakage at CPC concentration below 0.4 does not increases as pronounced as the surfactant leakage at higher CPC concentrations. This corresponds to the surface tension result, that is, at high [CPC] or high [CPC] to [PSS] ratio after the maximum concentration of the polymer-bound micelle is attained, the free surfactant concentration increases, resulting in the increase in surfactant leakage.

The effect of polymer and surfactant concentrations on Mg^{2+} and DCP rejections is shown in Fig. 7.6. The [CPC] to [PSS] ratio is kept constant at 1 to 2; the surfactant and polymer concentrations are varied accordingly. Rejection of Mg^{2+} is plotted as a function of PSS concentration as shown in Fig. 7.6; as PSS concentration increases from 2.5 mM to 100 mM, the Mg^{2+} rejection drastically increases at low PSS concentrations and gradually levels off at higher PSS concentrations. A maximum rejection of 97% is observed at 50 mM PSS. The same behavior is also observed for DCP; that is, as CPC concentration increases, the DCP rejection increases before leveling off. A maximum DCP rejection of 96% is observed at a surfactant concentration of approximately of 25 mM. The surfactant leakage as a function of CPC concentration is shown in Fig. 7.7. It is found that the surfactant leakage increases with increasing the initial CPC concentration.

At a constant initial Mg^{2+} concentration of 2.5 mM and a constant [CPC] to [PSS] ratio of 1 to 2, it is reasonable to expect an increase in anionic sites on the polyion chains per unit volume as the PSS concentration increase. A maximum Mg^{2+} rejection is achieved when the [Mg^{2+}] to [PSS] ratio approximately is 1 to 20 whereas a maximum DCP rejection is attained when [DCP] to [CPC] ratio approximately is 1 to 10. This suggested that the removal efficiency can be maximized by controlling [solute] to [colloid] ratio. However, the Mg^{2+} removal efficiency at this [CPC] to [PSS] ratio is as high as the efficiency at 0.4 [CPC] to [PSS] ratio as seen in Fig 7.3. As observed in the previous work[199], cac increases as electrolyte as well as polymer

concentrations increases; so we can expect to see the increase in surfactant leakage with increasing polymer concentration.

7.4.2 Kinematic Viscosity

Kinematic viscosity is plotted as a function of surfactant concentration at different salinities, as shown in Figs. 7.8 and 7.9. Fig. 7.8 shows the effect of the addition of NaCl and CPC on the kinematic viscosity of the polyelectrolyte at a fixed concentration of 50 mM. As seen in Fig. 7.8, the kinematic viscosity of the polyelectrolyte solution in the absence of salt exhibits strong dependence on the concentration of the surfactant. In the absence of salt, the kinematic viscosity drastically decreases as CPC concentration increases and tends to level off at higher CPC concentrations. The kinematic viscosity starts to level off at an approximate CPC concentration between 20 mM to 25 mM. The dependence of surfactant concentration on the kinematic viscosity is less pronounced for the systems with salt. At low surfactant concentration, a further decrease in the kinematic viscosity of the surfactant - polymer mixture is attained by adding salt, although the addition salt does not significantly change the kinematic viscosity of the surfactant-polymer mixtures at high surfactant concentrations.

Fig. 7.9 shows the effect of added salt and surfactant concentration on the kinematic viscosity of the polyelectrolyte solution at a constant [CPC] to [PSS] ratio of 1 to 2. The kinematic viscosity increases as the colloid concentration increases.

The kinematic viscosity is slightly reduced by the addition of salt. It should be noted that the experiments were performed at compositions where the surfactant and polymer do not precipitate.

The influence of additives (salt and surfactant) on the decrease in viscosity of polyelectrolyte is well known[195,201-204]. Due to the repulsive electrostatic forces between adjacent charges on the polyion chain, the chain has a highly extended conformation in additive-free solutions. The added salt or surfactant results in shielding of ionic groups on the polyions. Consequently, the polymer coils up and the coil dimension reduces and leads to a decrease in viscosity with increasing concentration of NaCl or CPC. However, it was found that the effect of surfactant on the reduction of the viscosity is stronger than the effect of simple salt[201]. It was explained that in the case of surfactant cations, the addition effect can be expected since they bind to the polyion chain cooperatively in the form of "polymer-induced" micelles. That is to say, the surfactant ions are not evenly distributed along the chain but they are rather localized in the form of smaller or bigger aggregates[87,205]. It is likely that the polyelectrolyte chain encircles the surfactant micelles to some extent and this is accompanied by a further decrease in dimension and viscosity. Due to the decrease in the kinematic viscosity by addition of surfactant, the addition of simple salt may not significantly affect the kinematic viscosity, primarily at high surfactant concentration regime as seen in Fig. 7.8. However, an opposite trend was observed in an anionic surfactant/cationic polymer mixture[206]; this study showed a marked increase in viscosity of cationic cellulose ether (polymer JR) solutions with added

sodium dodecylsulfate (SDS). This results from association of the alkyl chains of bound surfactant on separate polymer molecules, in effect generating a very high MW entity in solution. Moreover, it was observed that the kinematic viscosity levels off at a [CPC] to [PSS] ratio of 0.4-0.5; this is the ratio where we observe a maximum concentration of polymer-bound micelles (two anionic sulfonate PSS groups stabilize one aggregated cationic surfactant molecule[42]. As shown in previous work[42], as surfactant concentration increases above the cac, the number or concentration of the polymer-stabilized surfactant micelles increases, such micelles reduce the repulsion between the polyion chains, resulting in the decrease in the viscosity. However, the kinematic viscosity does not significantly decrease after this ratio because the increase in the concentration of the polymer-stabilized micelles is negligible.

At a constant [CPC] to [PSS] ratio of 1 to 2, the effect of the added salt on kinematic viscosity is slight, as shown in Fig. 7.9. It is commonly known that the viscosity increases as surfactant concentration increases as also seen in our previous work for CPC-only[19]. As the surfactant concentration increases, the surfactant micelles may change their size and shape from nearly spherical micelles to rodlike aggregates. For example, spherical to rod-like transition for CPC was observed at 0.3 M; also an increase of salt concentration leads to an increase in micellar length and consequently to a rise in viscosity[172]

7.4.3 Ultrafiltration Experiments

Flux is an important parameter in the economics of CEUF processes. Information about the dependence of the relative flux on colloid concentration can be used to calculate the gel point at which the flux becomes zero. Figs. 7.10 through 7.12 are semi-logarithmic plots between the relative flux and retentate CPC concentration, along with kinematic viscosity in the absence and presence of salt. The kinematic viscosity results are from Fig. 7.9. The relative flux is defined as flux of a sample divided by the flux of water or salt water. Previous studies showed that this semi-logarithmic plot is linear at high colloid concentration[18-19,44,135]. The CPC concentration where the flux is zero is called the gel concentration or gel point. The gel point at zero salt, 0.2 M NaCl, and 1 M NaCl is 500, 600, and 800 mM, respectively. Uchiyama and coworkers also observed that the gel point of CPC - PSS mixture in the absence of salt falls in this range[44]. It is seen that the decline in flux occurs concurrently with an increase in kinematic viscosity, as also seen in the previous work[19]. It should be note that the viscosity measurement was carried out at different solute concentration from the flux measurement. However, a previous study showed that the surfactant concentration, not the solute concentration, controls the solution viscosity and the flux[19].

It was found in previous work that in the case of CPC solutions without added polyelectrolyte, the gel point is 530 mM[16,19,207] where as the gel point in polyelectrolyte solution is 600 to 800 mM[135]. The gel point in the surfactant-polymer mixture in the absence of salt at a [CPC] to [PSS] ratio of 1 to 2 is approximately 500

mM CPC, corresponding to 1000 mM PSS. This remarkably indicates that the gel point occurs at a total colloid concentration, [PSS] + [CPC], of 1500 mM, as compared to gel points of 500 to 800 mM colloid for classical MEUF and PEUF (polyelectrolyte-enhanced ultrafiltration). Therefore, the presence of polyelectrolyte increases the flux of the colloid solutions, resulting in a higher obtainable CPC concentration before the flux becomes unacceptable low. Furthermore, the added salt further increases the gel point to a higher CPC concentration. This could be due to the observation of the slight reduction of the kinematic viscosity as salt is added. In addition, as mentioned earlier, the presence of salt can cause the micelles on a string to become more coiled; this can in fact reduce the contact area between the surfactant-polymer aggregates and the membrane, resulting in the increase in the flux.

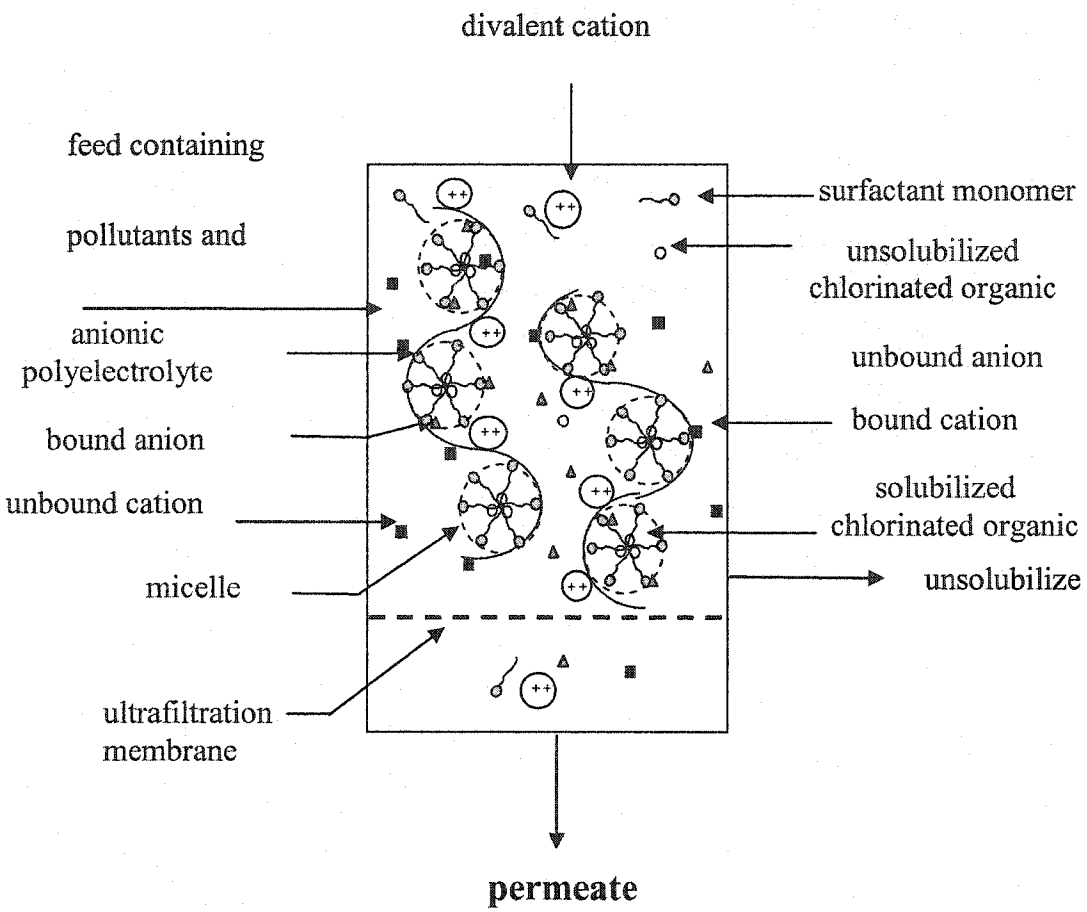


Figure 7. 1 Schematic of simultaneous removal of organic solute and divalent cation in polyelectrolyte micellar- Enhanced ultrafiltration (PE-MEUF).

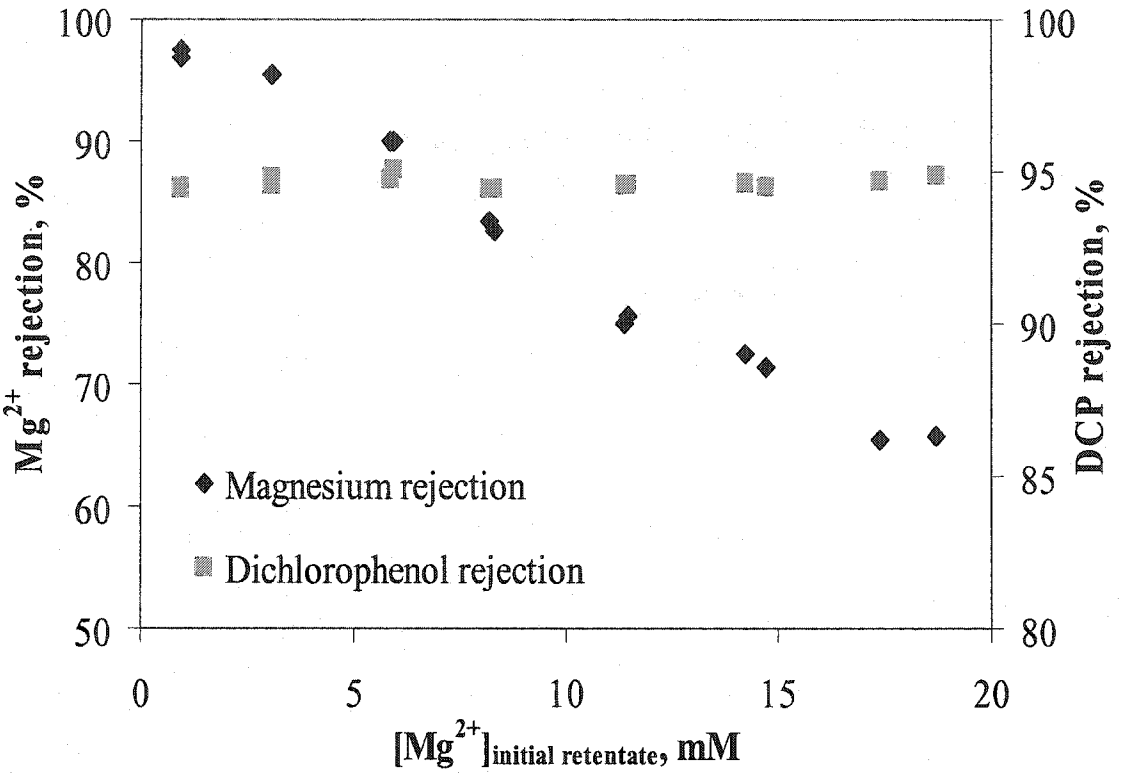


Figure 7. 2 Effect of Mg^{2+} concentration on Mg^{2+} and DCP rejections. [CPC] to[PSS] ratio is 25 mM to 50 mM. Initial [DCP] is 2.5 mM.

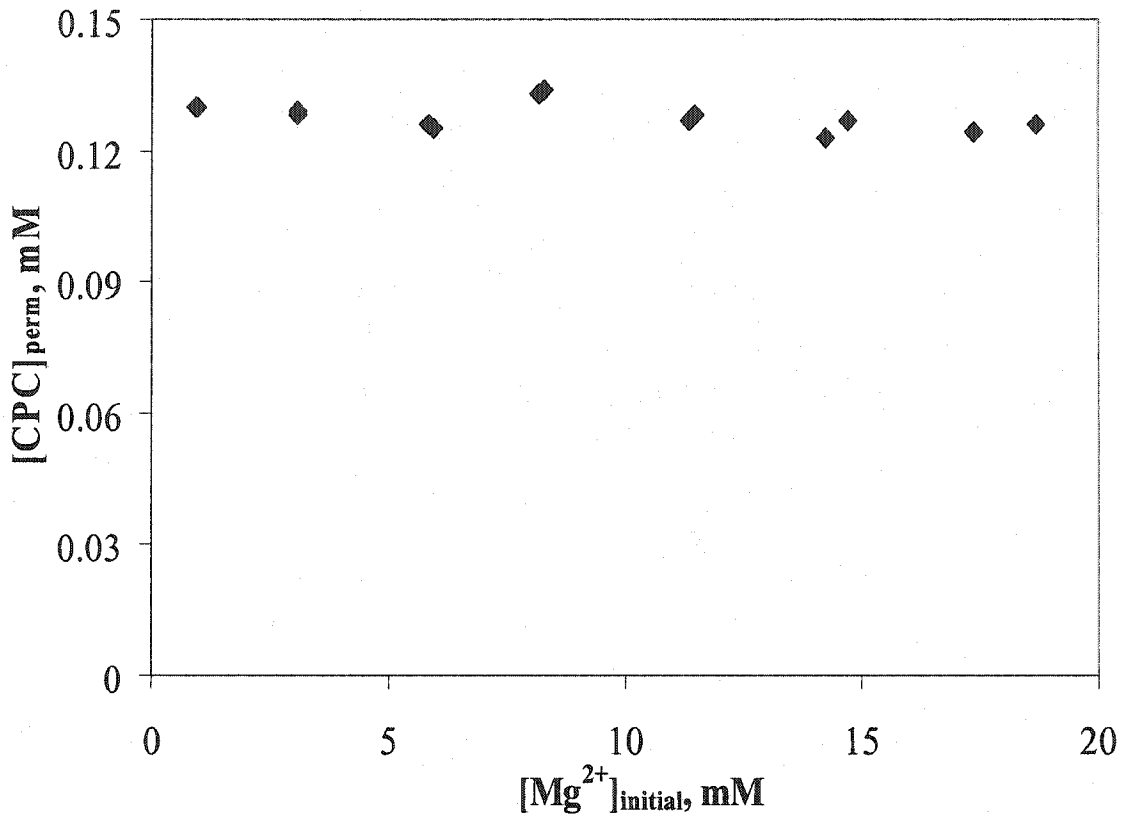


Figure 7. 3 Effect of Mg^{2+} concentration on the surfactant leakage. [CPC] to [PSS] ratio is 25 mM/50 mM. Initial [DCP] is 2.5 mM.

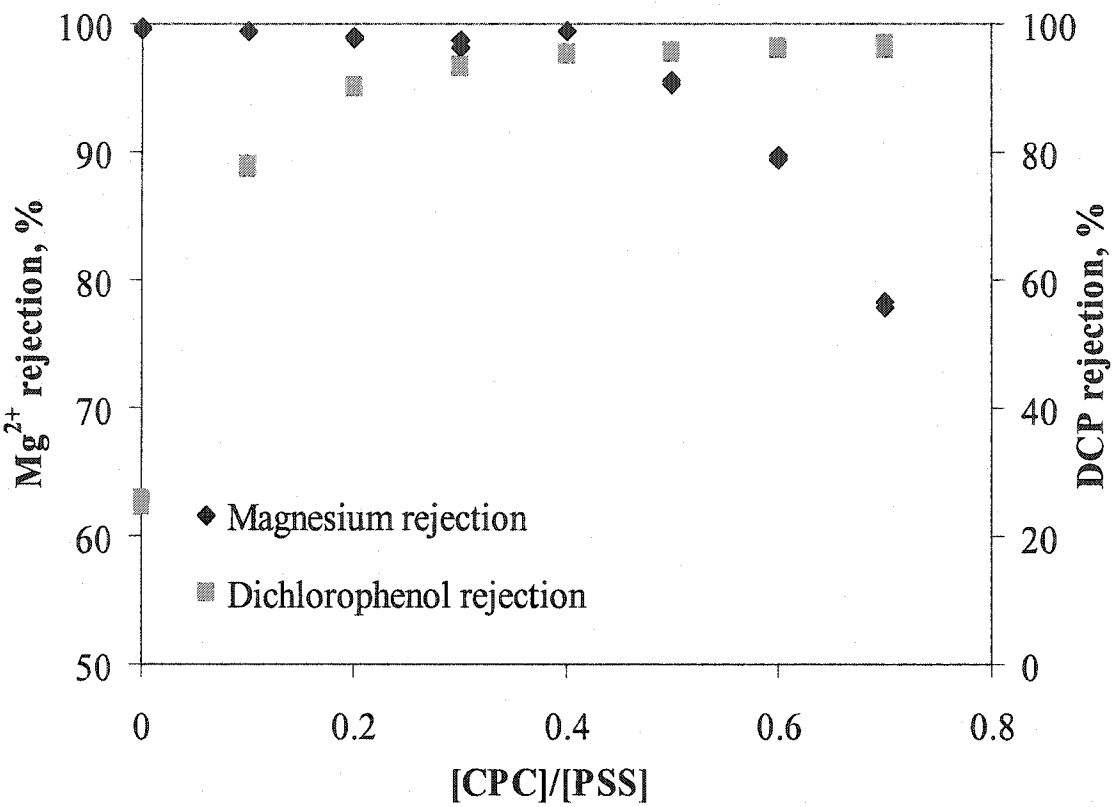


Figure 7. 4 Effect of [CPC] to [PSS] ratio on Mg^{2+} and DCP rejections. Initial [PSS] is fixed at 50 mM. Initial [DCP] and [Mg^{2+}] are both kept constant at 2.5 mM.

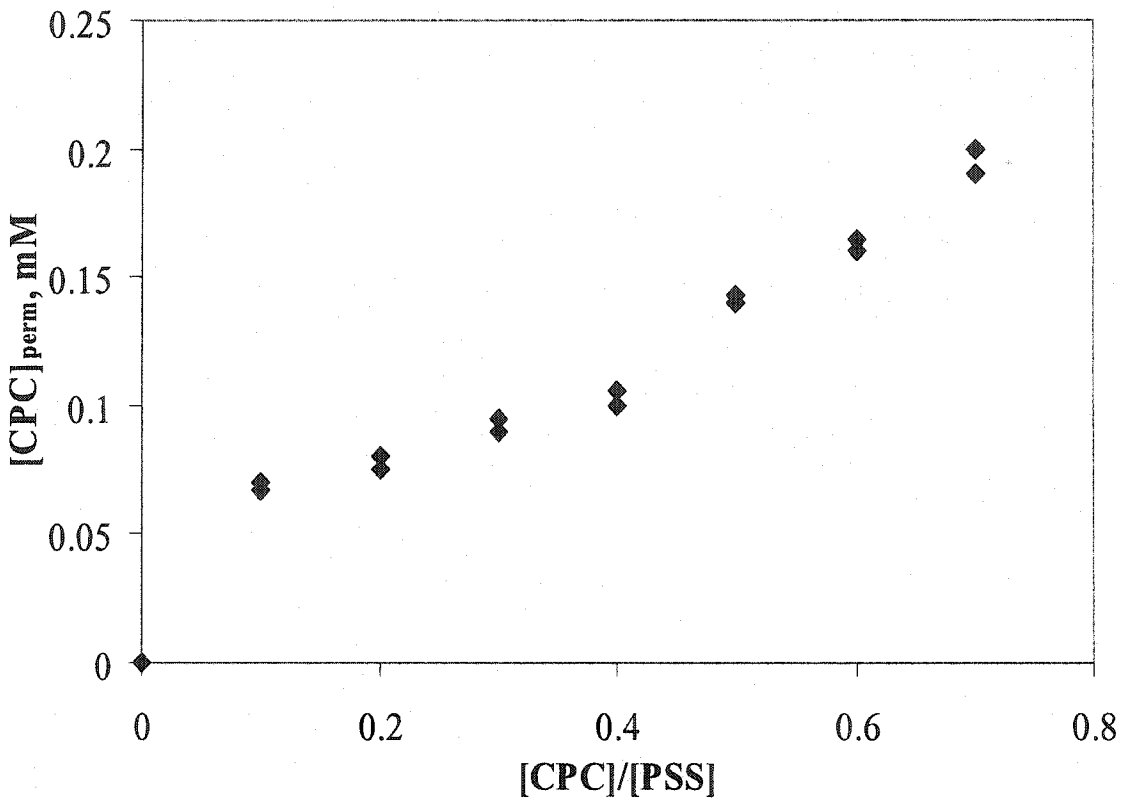


Figure 7. 5 Effect of [CPC] to [PSS] ratio on the surfactant leakage. Initial [PSS] is fixed at 50 mM. Initial [DCP] and $[Mg^{2+}]$ are both kept constant at 2.5 mM.

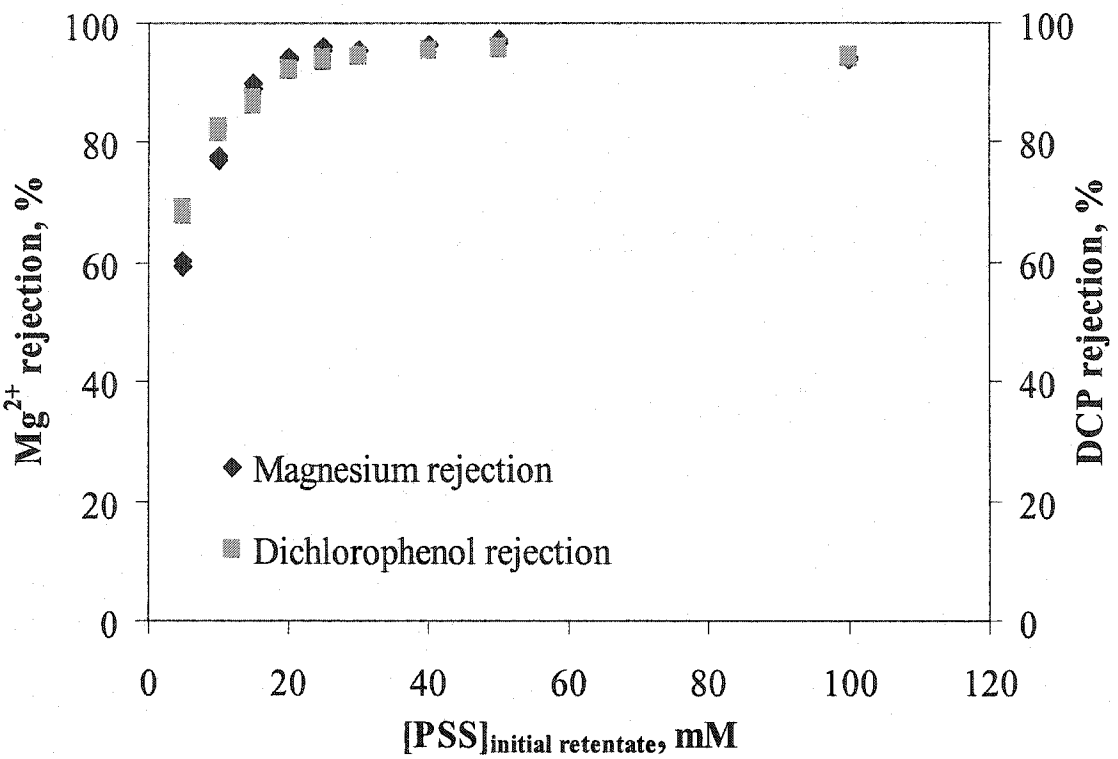


Figure 7. 6 Effect of PSS concentration on Mg^{2+} and DCP rejections. [CPC] to [PSS] ratio is 1/2. Initial [DCP] and [Mg^{2+}] are both kept constant at 2.5 mM.

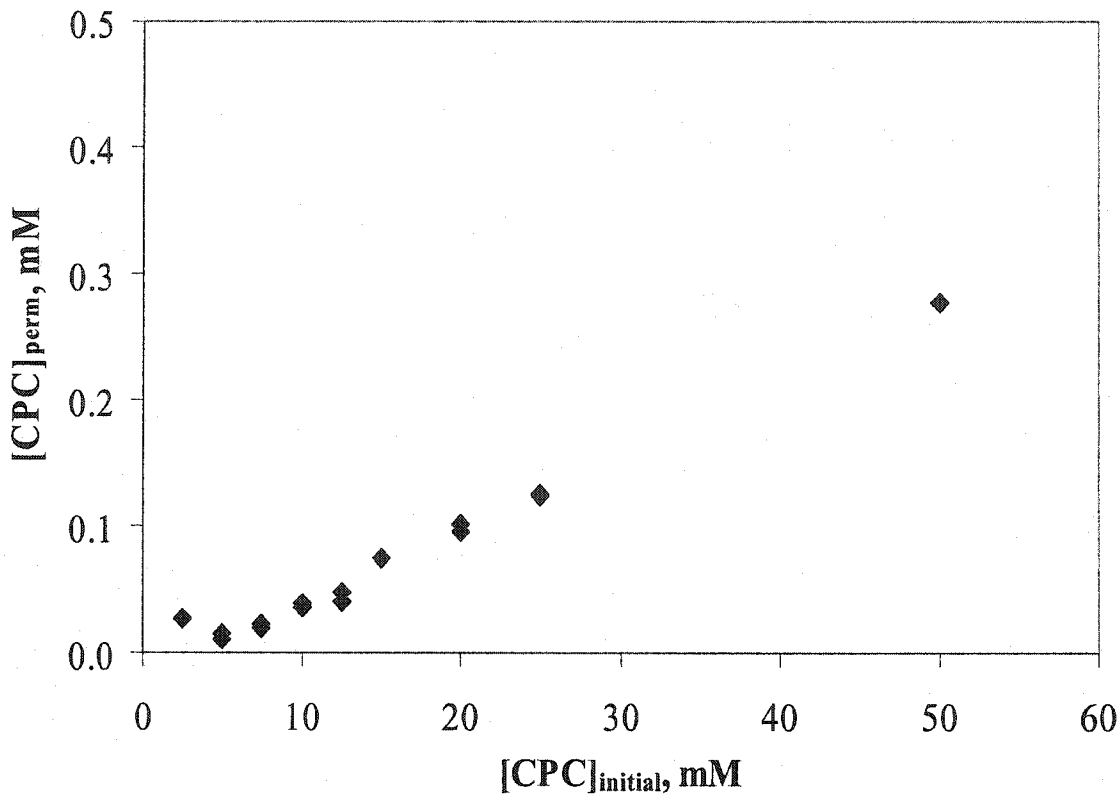


Figure 7. 7 Effect of CPC concentration on the surfactant leakage. [CPC] to [PSS] ratio is 1/2. Initial [DCP] and [Mg^{2+}] are both kept constant at 2.5 mM.

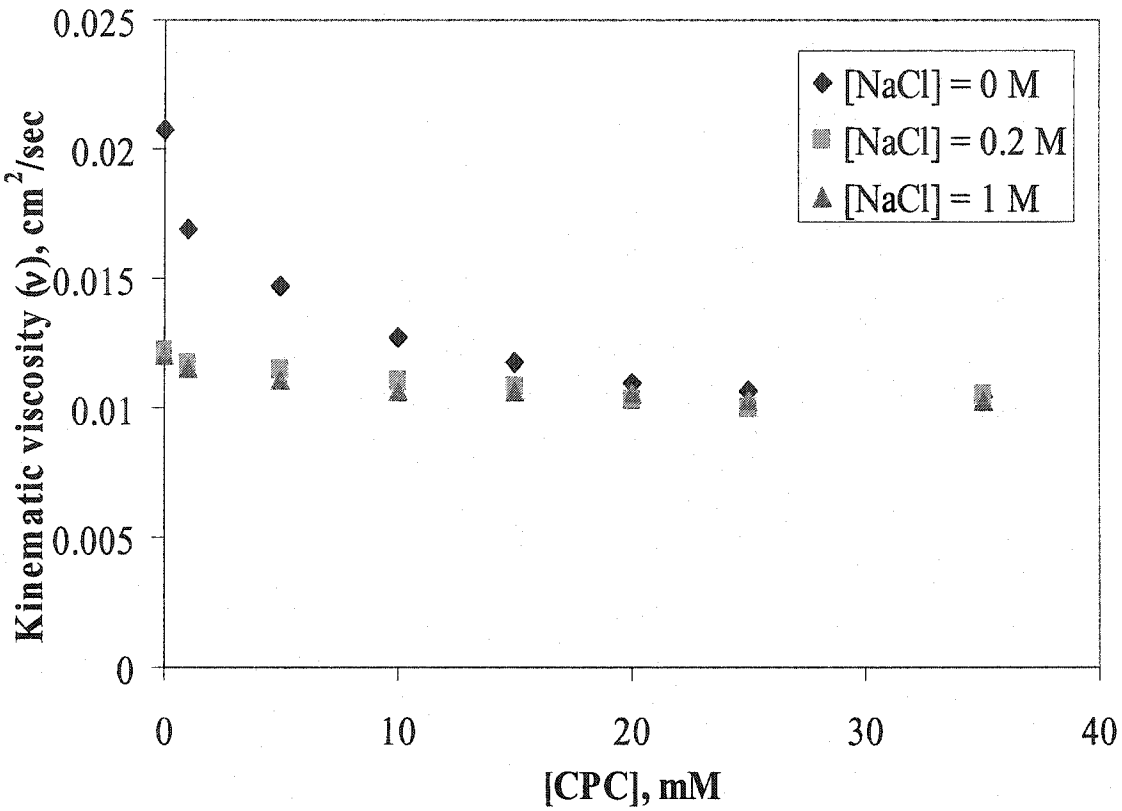


Figure 7. 8 Kinematic viscosity of PSS solutions at different CPC concentration in the presence and absence of NaCl. [PSS] is kept constant at 50 mM. [DCP] to[CPC] and [Mg^{2+}] to [PSS] ratios are 1/10 and 1/20, respectively.

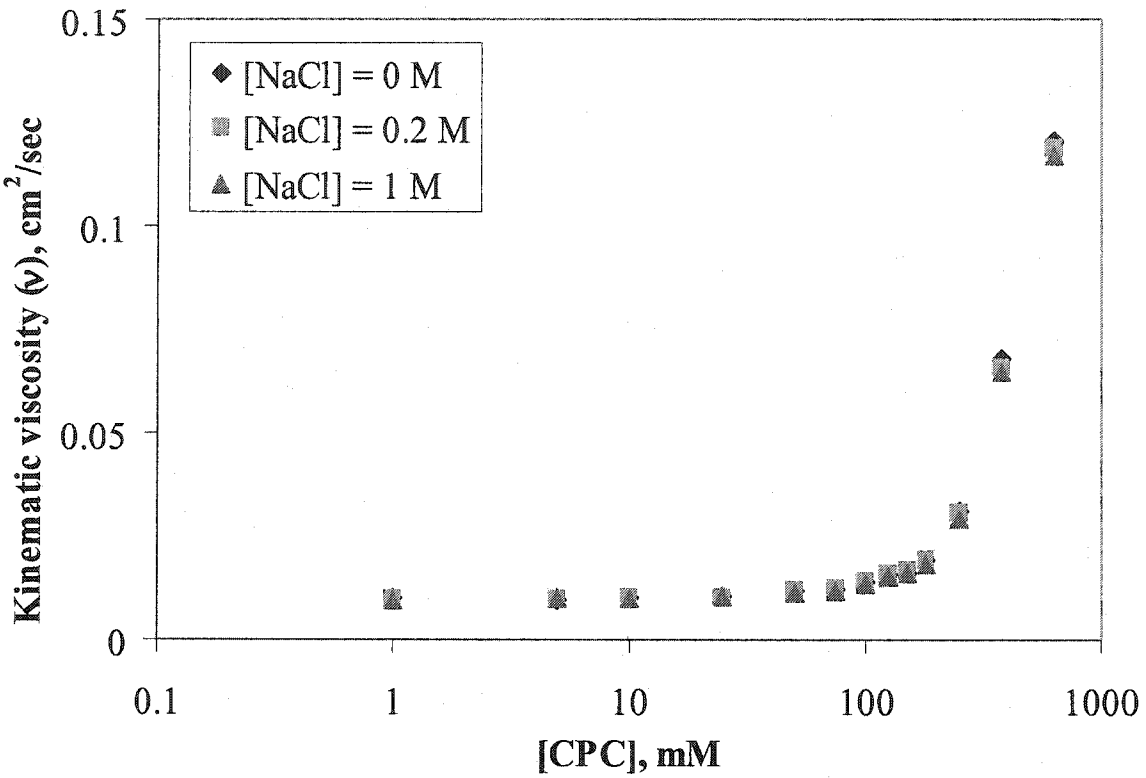


Figure 7. 9 Kinematic viscosity of PSS solutions at different CPC concentration in the presence and absence of NaCl. [CPC] to[PSS] ratio is kept constant at 1/2. [DCP] to [CPC] and [Mg^{2+}] to [PSS] ratios are 1/10 and 1/20, respectively.

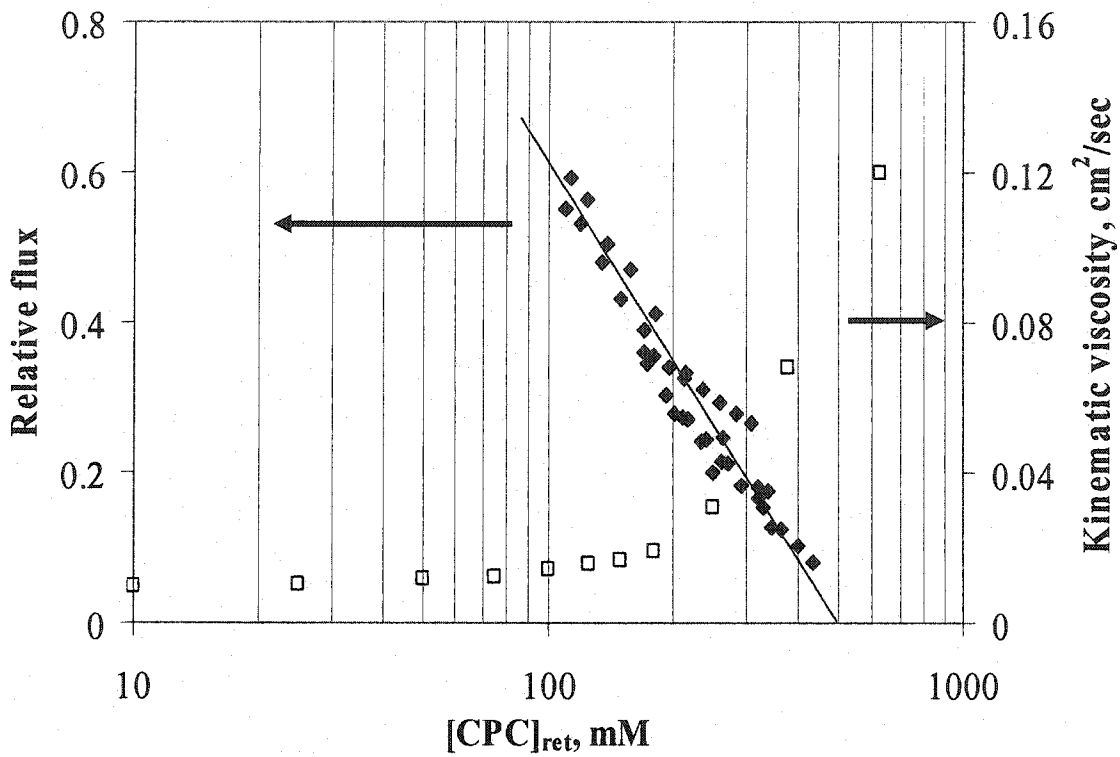


Figure 7. 10 Relative flux and kinematic viscosity of surfactant to polymer mixtures as a function of [CPC] in the absence of NaCl. Initial [DCP] to [CPC] and $[Mg^{2+}]$ to [PSS] ratios are 1/10 and 1/20, respectively.

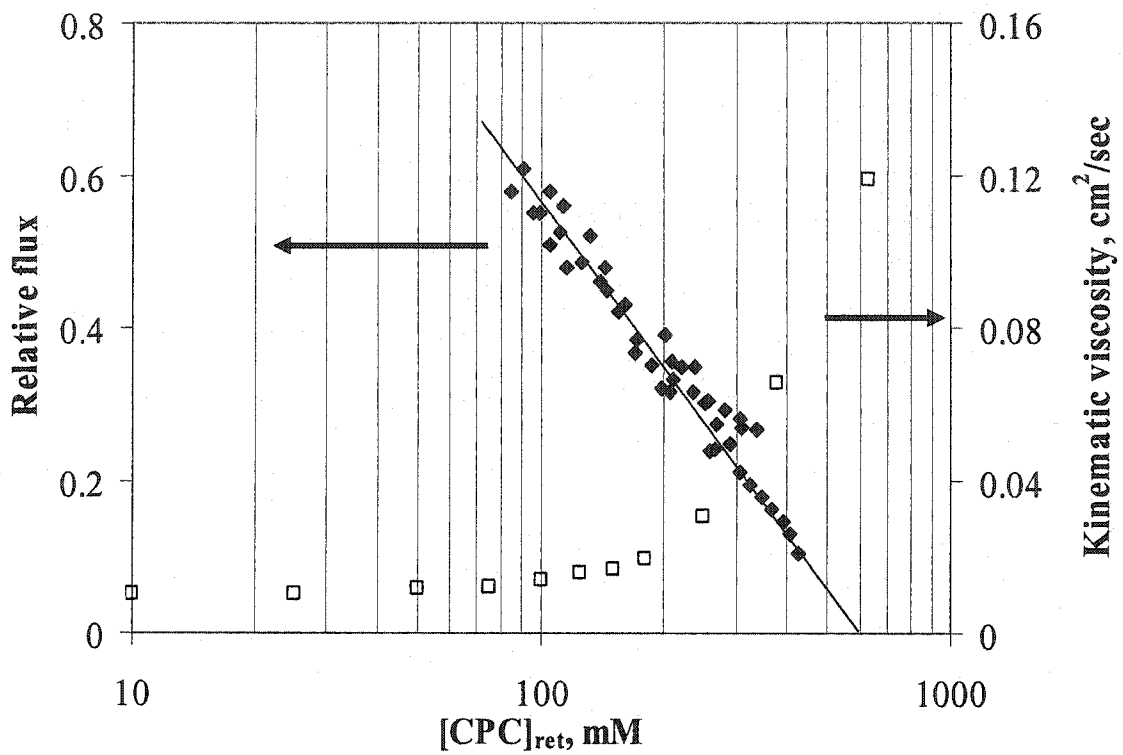


Figure 7. 11 Relative flux and kinematic viscosity of surfactant - polymer mixtures as a function of [CPC] in the presence of 0.05 M NaCl. Initial [DCP] to [CPC] and $[Mg^{2+}]$ to [PSS] ratios are 1/10 and 1/20, respectively.

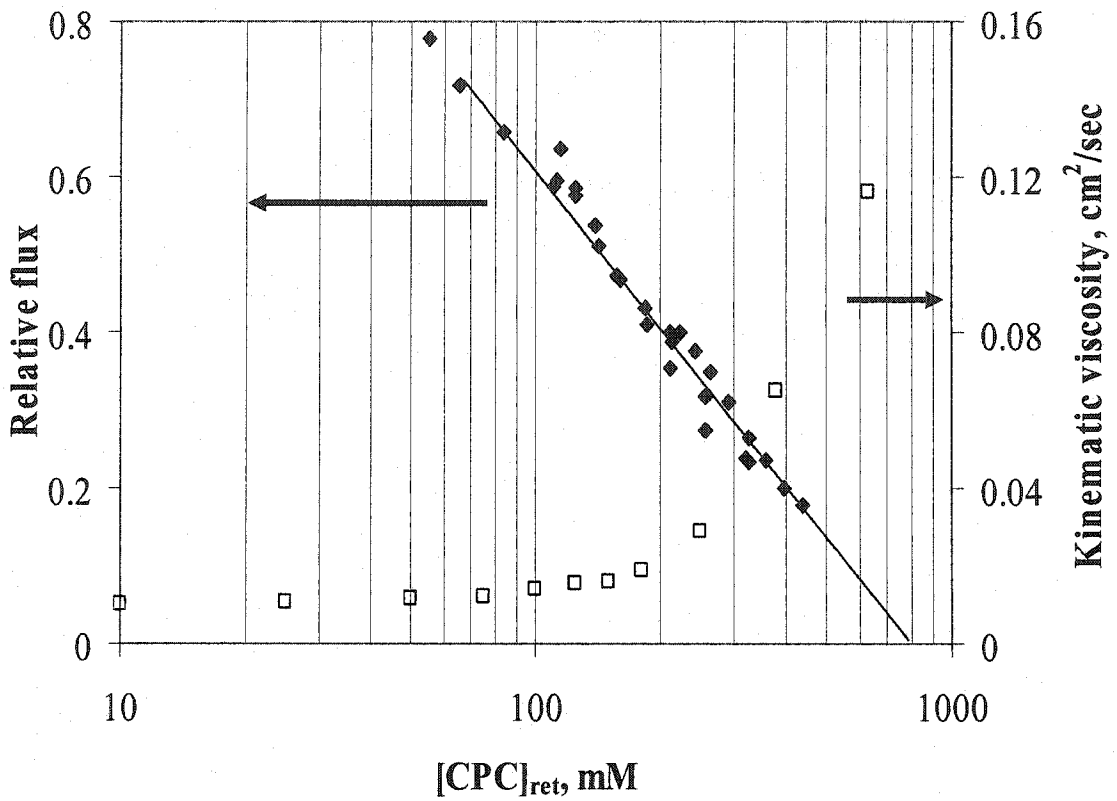


Figure 7. 12 Relative flux of surfactant - polymer mixtures in the presence of 1 M NaCl. Initial [DCP] to [CPC] and $[Mg^{2+}]$ to [PSS] ratios are 1/10 and 1/20, respectively.

CHAPTER 8

CONCLUSIONS AND FUTURE PERSPECTIVES

8.1 Conclusions

The first study evaluated removal of 2-monochlorophenol (MCP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) using n-hexadecyl pyridinium chloride or cetylpyridinium chloride (CPC) and a mixture of CPC and poly(styrenesulfonate) (PSS) to compare the removal efficiency of the surfactant-only solutions and the surfactant-polymer mixtures. The surfactant-only system was shown to be more effective than the surfactant-polymer systems to remove all three solutes. Among three solutes, TCP with the lowest water solubility was removed most effectively, as compared to MCP and DCP. The rejection of TCP and DCP was encouraging, but multistage operation might be necessary for MCP removal. The surfactant leakage was remarkably reduced in the presence of polymer. Minimum surfactant leakage was found in the system studied with the highest hydrophobicity solute which is TCP.

The second study determined (1) apparent acid dissociation ($K_{a,app}$) of the three phenolic solutes in the surfactant-only solutions and the surfactant-polymer mixtures at different salinities, (2) the effect of solute species (neutral or charged species) on the distribution coefficients into the surfactant micelles and surfactant-polymer aggregates

as well as the solubilization constants. It was found that for a given solute, pK_a values are dependent on the type of colloids and follow the order $pK_{a,micelle} < pK_{a,water} < pK_{a,surfactant - polymer}$. The addition of salt in the micellar solution was shown to increase the $pK_{a,app}$ value for a given phenolic solute while it does not significantly influence the $pK_{a,app}$ value in the surfactant-polymer mixtures. The distribution coefficient of the phenolate anion in the micellar solution is shown to be higher than that of the neutral speices. Therefore, a higher solute removal can be expected in a micellar solution at higher pH than at lower pH.

The third and the fourth studies investigated the effect of salinity on the solubilization and surfactant leakage, respectively, in surfactant-only and surfactant-polymer systems. Surface tension measurement was used to determine critical aggregation concentration (cac) which helped to explain the increase in the surfactant leakage in the surfactant-polymer mixtures as the salt concentration increased. Unlike the surfactant-polymer mixtures, in the micellar solution, the addition of salt was found to improve the process efficiency in terms of increasing the solubilization constants and reducing the surfactant leakage into the permeate.

Finally, the last study dealt with the simultaneous removal of magnesium ion and TCP using a mixture of CPC and an excess amount of PSS, forming net negatively charged surfactant – polymer aggregates. It was found that the use of the surfactant – polymer aggregates to remove the metal ion was effective, even though the organic solute was present. Both colloid concentration and the surfactant to polymer concentration ratio are important parameters for the process efficiency. An

additional study was the effect of salinity on gel point. It was found that the presence of salt helped to increase the gel point, which means that the process can be operated at relatively high colloid concentration before observing an unacceptable low flux.

8.2 Future Perspectives

Most of the systems investigated within this work employed micellar and surfactant – polymer aggregates to remove organic solutes were one component system (one organic solute was studied at the time). In the real world, the contaminated water contains a mixture of organic solutes. Therefore, it might be desired to study the removal efficiency of this CEUF technique for a mixture of MCP, DCP, and TCP or other possible solutes. It is also interesting to investigate other types of non process elements (NPEs) such as Cu and Mg or mixtures of them because these metal ions are sensitive to pH; they can undergo hydrolysis at a certain pH.

Further development of the CEUF technique such as using a mixture of anionic surfactant and a cationic polymer could demonstrate the separation of multivalent anionic species such as multivalent arsenic that might be present with organic solute. It may be necessary to conduct CEUF as a multiple stage process in order to achieve a required objective separation, especially for a solute with high water solubility, such as MCP. For example, the rejection of MCP in a surfactant – polymer mixture is 76%. Two stages in series reducing the phenolic level at similar surfactant loading concentration could increase the overall rejection to 96%. In addition, it might be

worth studying this staged process using a continuous membrane unit as would be used industrially. The continuous ultrafiltration unit (e.g., a spiral wound model) could also be used to compare gel point results to those observed in this work for batch operations.

The effect of the solutes, including the phenolic solutes and the metal ion, on the cac would be interesting to measure and compare to permeate concentrations reported here. Since the organic solutes are sensitive to pH in that they can deprotonated at high pH levels, it might be desirable to study the effect of pH on the CMC as well as the cac.

Finally, these studies left open several questions regarding the recovery of separation agents (such as surfactant and polymer) for recycle and reuse. The recycle can be crucial for an economical process, so it needs to be developed and combined with the ultrafiltration unit operation in an integrated pilot plant demonstrating the ability of overall process to efficiently clean-up pulp and paper industry wastewater

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